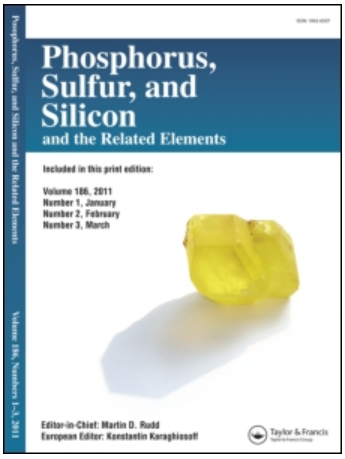

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HIGHLY SELECTIVE ASYMMETRIC INTRAMOLECULAR SELENOCYCLISATION

Hiroya Takada, Yoshiaki Nishibayashi, Sanjay Kumar Srivastava, Kouichi Ohe and Sakae Uemura*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Asymmetric intramolecular selenocyclisation of alkenoic acids, alkenols and alkenyl urethanes using chiral ferrocenylselenenyl cations proceeds smoothly to give the corresponding lactones, cyclic ethers and N-heterocyclic compounds, respectively, in moderate yields with very high diastereoselectivities.

KEYWORDS: diselenide, selenocyclisation, alkenoic acids, alkenols, alkenyl urethanes

INTRODUCTION

A substantial amount of literature concerning asymmetric cyclisations has recently emerged in which diastereoselective halogenocyclisations are especially useful for the synthesis of chiral heterocyclic compounds and for the functionalisation of a double bond. Although an intramolecular selenocyclisation has been widely used for preparing the heterocyclic compounds such as selenolactones and selenoethers in high yields, the studies on its asymmetric version have just started.[1] Some of us recently succeeded in highly diastereoselective methoxyselenenylation of alkenes using chiral ferrocenylselenenyl bromide prepared *in situ* from chiral diferrocenyl diselenide and bromine. We now report the details of our approach to the asymmetric

intramolecular selenocyclisation of alkenoic acids, alkenols and alkenyl urethanes using chiral ferrocenylselenenyl cations.[1d]

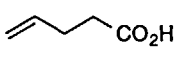
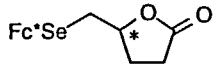
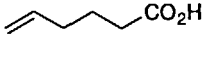
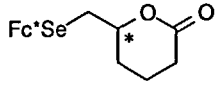
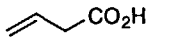
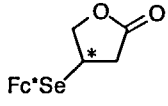
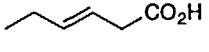
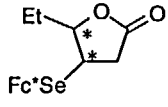
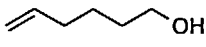
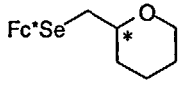
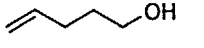
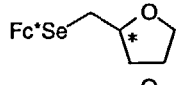
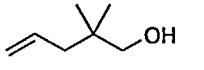
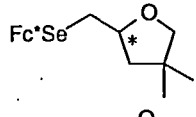
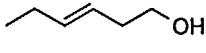
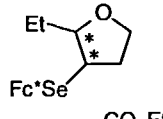
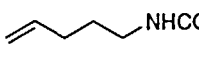
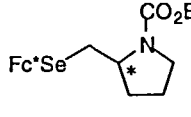
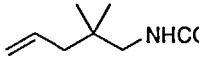
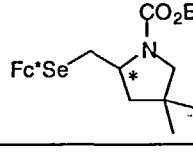
RESULTS AND DISCUSSION

For example, the asymmetric selnocyclisation of 4-pentenoic acid **1a** was performed as follows. The chiral [*R,S*; *R,S*]-diferrocenyl diselenide was converted *in situ* into the chiral (*R,S*)-ferrocenylselenenyl bromide by treatment with bromine in CH_2Cl_2 at -78 °C, and after 15 min silver hexafluorophosphate ($AgPF_6$) was added and the stirring was continued for 15 min. Then a CH_2Cl_2 solution of 4-pentenoic acid was added at -78 °C. After 1 h, the mixture was slowly warmed to room temperature (for 30 min) and it was stirred for another 3.5 h. The product (*R,S*)-**2a** was isolated in a high yield with an excellent diastereoselectivity after purification by column chromatography on silica gel using a mixture of hexane : AcOEt : Et_3N = 8 : 2 : 1 as an eluent. The diastereomeric excess of (*R,S*)-**2a** was determined by ^{1}H-NMR integration of the singlet methyl proton resonance of the NMe_2 group in its crude product. The use of the chiral (*S,R*)-ferrocenylselenenyl hexafluorophosphate (Fc*$SePF_6$) derived *in situ* from [*S,R*; *S,R*]-ferrocenylselenenyl bromide and silver hexafluorophosphate resulted in a formation of the expected (*S,R*)-**2a** in a high yield with an excellent diastereoselectivity. The typical results are shown in Table I. On the other hand, in the case of intramolecular etherification of the alkenols **1e-h**, the corresponding (*R,S*)-[**2e-h**] were obtained in excellent yields (also in Table I).

On the other hand, intramolecular cyclisation of alkenyl urethanes **1i** proceeded with (*S,R*)-ferrocenylselenenyl hexafluorophosphate with a moderate diastereoselectivity. However, when the counter anion PF_6^- was replaced by BF_4^- using silver tetrafluoroborate ($AgBF_4$), the product **2i** was obtained in a moderate

yield with an excellent diastereoselectivity (also in Table I). These results showed that the counter anion of chiral ferrocenylselenenyl moiety played an important role for stereoselection of the produced N-heterocyclic compounds.

Table I. Selonocyclisation using Fc*SePF$_6$[a] or Fc*SeBF$_4$[b]

Substrate 1		Product 2		Yield (%)[c]	de (%)[d]
	1a		2a	91[a]	>95
	1b		2b	87[a]	89
	1c		2c	76[a]	33
	1d		2d	93[a]	>95
	1e		2e	96[a]	66
	1f		2f	97[a]	>95
	1g		2g	95[a]	89
	1h		2h	89[a]	>95
	1i		2i	67[b]	>99
	1j		2j	72[b]	56

[a]The reactions were performed in CH_2Cl_2 at 25 °C for 4 h. [b]The reactions were performed in CH_2Cl_2 at 25 °C for 20 h. [c]Isolated yield. [d]The de was measured by ^{1}H NMR integration.

Scheme 1. Plausible Scheme for Approach of Chiral Se Species

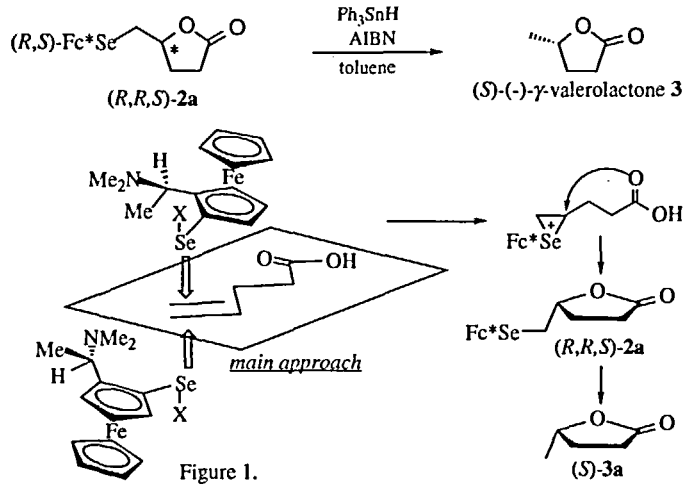


Figure 1.

Reductive cleavage of chiral ferrocenylselenium moiety of (*R*,*S*)-**2a** with Ph3SnH in toluene afforded the lactone **3** which has *S* configuration at the chiral centre (Scheme 1). This means the absolute configuration of (*R*,*S*)-**2a** to be (*R*,*R*,*S*) and, consequently, (*S*,*R*)-**2a** to be (*S*,*S*,*R*)-**2a**, showing that the diastereoselective reaction might proceed as shown in Figure 1. A chiral (*R*,*S*)-ferrocenylselenenyl hexafluorophosphate (Fc*SePF$_6$) approaches the C=C moiety **1a** from the less hindered direction (a front side approach) to afford a chiral episelenonium ion in which an intramolecular back side attack of the carboxylate anion occurs to afford the product (*R*,*R*,*S*)-**2a**. The method presented here might be useful for preparing the chiral heterocyclic compounds.

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