Asymmetric Baeyer–Villiger Oxidation of Cyclic Ketones Using Chiral Organoselenium Catalysts

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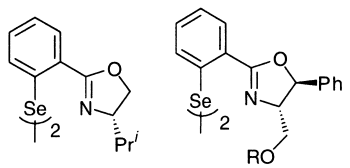
Novel optically active diselenides having a chiral oxazoline have been prepared and the structure of one of them is unambiguously determined by X-ray structural analysis. Treatment of a variety of cyclobutanones with 30% H_2O_2 in the presence of a catalytic amount of the optically active diselenides in tetrahydrofuran or 1,4-dioxane at 0 °C–rt affords the corresponding γ-lactones in up to 92% yield with up to 19% ee. The enantioselectivity of the product is not yet satisfactory, but this is the first example of asymmetric Baeyer–Villiger oxidation catalyzed by chiral organoselenium compounds.

Baeyer–Villiger oxidation is one of the most valuable methods for the transformation of ketones into the corresponding esters.[1] Especially, the oxidation of cyclic ketones is widely used for the synthesis of lactones. In the last decade, transition metal-catalyzed Baeyer–Villiger oxidation[2] using clean oxidants such as molecular oxygen[3] and hydrogen peroxide[4] has been developed and studied extensively. In contrast, asymmetric Baeyer–Villiger oxidation has been limited until recently to the use of biocatalysts[5] such as enzymes obtained from various microorganisms. However, since the first example of the transition metal-catalyzed asymmetric Baeyer–Villiger oxidation of cyclic ketones was reported independently by Bolm et al.[6a] and Strukul et al.,[7a] nonenzymatic asymmetric Baeyer–Villiger oxidation has been intensively studied by several groups.[6–8]

Peroxyseleninic acid ($RSe(O)O_2H$), obtained by oxidation of seleninic acid ($RSeO_2H$) with oxidants, is known to be an effective oxidant for epoxidation of alkenes[9] and Baeyer–Villiger oxidation of ketones.[9c,10] However, no successful report on the asymmetric Baeyer–Villiger oxidation using peroxyseleninic acid has appeared so far.[11] We have so far developed preparative methods for a variety of optically active organoselenium compounds such as selenoxides, selenimides and selenium ylides and utilized them in several asymmetric reactions where a chiral center on the selenium atom is a key point to obtain the chiral organic compounds.[12] We now report the results of the asymmetric Baeyer–Villiger oxidation of cyclic ketones catalyzed by chiral organoselenium compounds in which peroxyseleninic acid is an oxidant for the catalytic transformation.

Results and Discussion

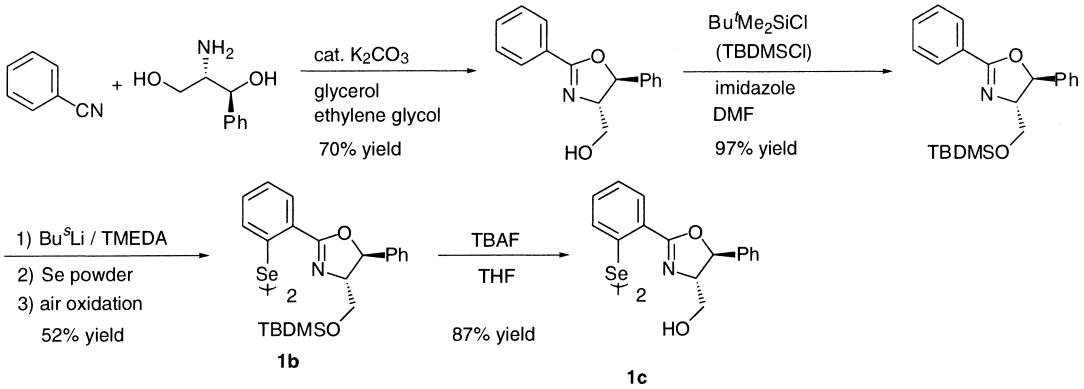
At first, we prepared several optically active diselenides **1** (Chart 1) having a chiral 2-oxazoline, because the corresponding peroxyseleninic acids generated in situ from **1** may be used for asymmetric Baeyer–Villiger oxidation. Chiral diselenide **1a** has been prepared by Wirth and co-workers.[13] Novel diselenides (**1b** and **1c**) were prepared from the corresponding chiral 2-phenyl-2-oxazolines in several steps as shown in Scheme 1. The molecular structure of the diselenide **1c** was unambiguously clarified by X-ray structural determination, an ORTEP drawing of which is shown in Fig. 1. From the X-ray analysis, the distances between the selenium atom and the nitrogen atom of 2-oxazoline ring were revealed to be Se1–N1 = 2.69 Å and Se2–N2 = 2.89 Å, which were shorter than the sum of van der Waals radii of Se and N (3.45 Å).[14] This result suggests the existence of Se···N interaction, as has been reported.[12d,15]



1a **1b**; R = TBDMS **1c**; R = H

Chart 1. Optically active diselenides.

Next, asymmetric Baeyer–Villiger oxidation of 3-phenylcyclobutanone (**2a**) with 30% H_2O_2 aqueous solution was carried out in tetrahydrofuran (THF) at room temperature in the presence of a catalytic amount of chiral diselenides **1** (Eq. 1). Typical results are shown in Table 1. In all cases, the corresponding lactone (**3a**) was obtained in good yields, but unfortunately with low selectivities (Table 1, Entries 1, 2 and 3). Separately, it was confirmed that no reaction proceeded in the absence of **1**. The addition of $Sc(OTf)_3$ (0.02 molar amounts to the ketone) as Lewis acid improved the yield of **3a**, but no improvement of enantioselectivities was observed (Entries 4, 5 and 6). Interestingly, the addition of $Yb(OTf)_3$ (0.02 molar amounts) to the reaction system by using **1b** slightly improved the enantioselectivity of **3a** up to 13% ee (Table 1, Entry 8). On the other hand, no influence was observed in the reaction using **1a** (Table 1, Entry 7). These results suggest that the coordination



Scheme 1. Preparation of optically active diselenides.

Table 1. Asymmetric Baeyer–Villiger Oxidation of 3-Phenylcyclobutanone (**2a**)[a)]

Entry	Cat.	Lewis Acid	Solvent	Yield/%	Ee/%
1	**1a**	—	THF	66	5
2	**1b**	—	THF	84	6
3	**1c**	—	THF	77	3
4	**1a**	$Sc(OTf)_3$	THF	100	0
5	**1b**	$Sc(OTf)_3$	THF	100	4
6	**1c**	$Sc(OTf)_3$	THF	100	7
7	**1a**	$Yb(OTf)_3$	THF	88	0
8	**1b**	$Yb(OTf)_3$	THF	91	13
9	**1c**	$Yb(OTf)_3$	THF	79	7
10	**1b**	$Yb(OTf)_3$	1,4-dioxane	92	15
11	**1b**	$Yb(OTf)_3$	1,2-dimethoxyethane	75	10
12[b)]	**1b**	$Yb(OTf)_3$	THF	54	19
13[c)]	**1b**	$Yb(OTf)_3$	THF	31	12

a) Reaction conditions; **2a** (0.50 mmol), cat. (0.0050 mmol), Lewis acid (0.010 mmol), 30% aq H_2O_2 (75 μL), pH 7.4 phoshate buffer solution (10 μL), solvent (1 mL), at room temperature for 24 h. b) At 0 °C. c) At −20 °C.

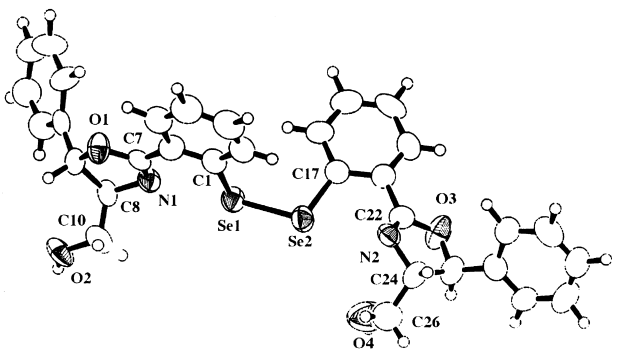
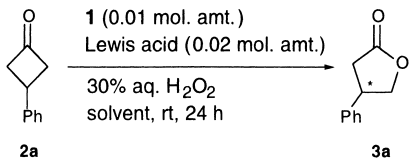


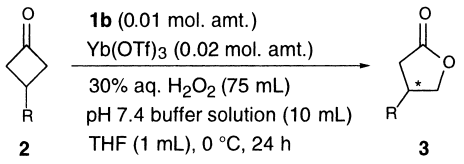
Fig. 1. The ORTEP drawing of optically active diselenide **1c**. Selected bond lengths, angles, torsion angle (Å, deg, deg): Se1–Se2 = 2.333(1); C7–N1 = 1.25(1); C22–N2 = 1.22(1) O1–C7–N1 = 119.5(8); O3–C22–N2 = 119.4(10); C1–Se1–Se2–C17 = −85.7(4).

of the Yb atom with both the oxygen atom on the seleninic or peroxyseleninic acid moiety and the oxygen atom on the silyl ether moiety might change the structure of a reactive intermediate, resulting in an improvement of the enantioselectivity of **3a**. Reactions in the presence of diselenide **1b** (0.01 molar amount to the ketone) and $Yb(OTf)_3$ were then investigated under several reaction conditions. Similar results were obtained in other solvents such as 1,4-dioxane and 1,2-dimethoxyethane (Table 1, Entries 10 and 11). The best enantioselectivity (19% ee) was obtained in the oxidation of **2a** at 0 °C to give **3a** in 54% yield (Table 1, Entry 12).

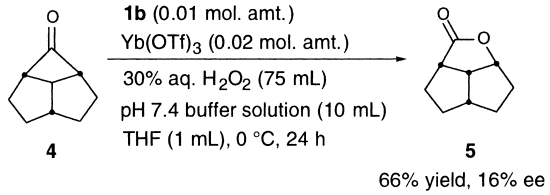


(1)

Treatment of other 3-substituted cyclobutanones **2b** and **2c** with H_2O_2 in the presence of **1b** afforded the corresponding lactones **3** with similar enantioselectivities (Eq. 2). The Baeyer–Villiger oxidation of tricyclic ketone **4**[6d,16] was also investigated, the corresponding lactone **5** being obtained in 66% yield with 16% ee (Eq. 3). When kinetic resolution of racemic 2-phenylcyclohexanone (**6**) and bicyclooctanone (**8**) was examined, the corresponding lactones (**7** and **9**) were obtained, but no asymmetric induction was observed in both the recovered ketones and the produced lactones (Eqs. 4 and 5).



(2)



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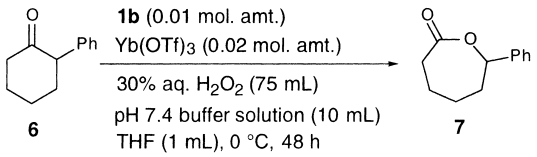
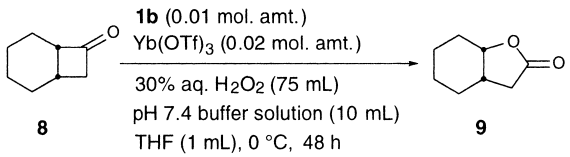
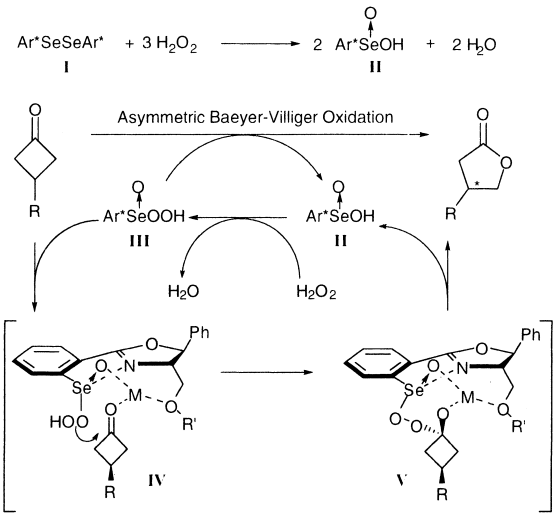


(4)



(5)

A plausible reaction pathway is shown in Scheme 2. Treatment of $(Ar^*Se)_2$ (I) with H_2O_2 affords a chiral arylseleninic acid (II) which is further oxidized to the corresponding arylperoxyseleninic acid (III).[10d] The coordination of the carbonyl oxygen atom of cyclobutanone and the two oxygen atoms of III to the Yb atom (M) generates the intermediate IV. The attack of the peroxyseleninic acid moiety in IV to the carbonyl carbon atom gives the intermediate V followed by the rearrangement to give the corresponding γ-lactones together with the formation of II. Asymmetric induction should occur at the rearrangement step. In our catalytic oxidation system, two diastereoisomers each of seleninic and of peroxyseleninic acid could be formed because seleninic and peroxyseleninic acids have a tricoordinate geometry with central chirality on the selenium atom. Not only the chirality on the oxazoline ring but also the central chirality on the selenium atom may have an effect on enantioselectivity. Quite recently, Kamigata et al. succeeded in the optical resolution of racemic seleninic acid and described that the racemization of the resolved seleninic acid proceeded easily in a dilute solution.[17] The existence of Se···N interaction in the intermediates IV and V might be expected to lock the conformation of the intermediates and prevent slightly



Scheme 2. Plausible pathway of asymmetric Baeyer–Villiger oxidation.

the racemization because of thermodynamical stabilization[18] of the peroxyseleninic acid, and so the enantio-enriched γ-lactone is obtained (up to 19% ee). Highly stereoselective formation of seleninic and peroxyseleninic acids should be essential for achieving a high asymmetric induction.

Experimental

General Procedures. ^{1}H and ^{13}C-NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300, and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with Shimadzu GC-14A instrument equipped with a CPB 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 mm film thickness) column using helium as carrier gas. GLC yields were determined using cyclododecane as an internal standard. HPLC analyses were carried out on a HITACHI L-7100 with an L-7300 column oven and an L-7400 UV detector using a Daicel Chiralcel OD column. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-SX102A spectrometer. Column chromatographies were performed with Merck silica gel 60. (4*S*,5*S*)-2-(4-*tert*-Butyldimethylsiloxymethyl-5-phenyl-2-oxazolinyl)benzene was prepared by the reported method.[19]

Preparation of Bis{2-[(4*S*,5*S*)-4-(*tert*-butyldimethylsiloxymethyl)-5-phenyl-2-oxazolinyl]phenyl} Diselenide (1b). *sec*-Butyllithium (23.0 mL of 1.06 M cyclohexane–hexane solution, 24.4 mmol) was added to a stirred solution of (4*S*,5*S*)-2-(4-*tert*-butyldimethylsiloxymethyl-5-phenyl-2-oxazolinyl)benzene (7.78 g, 21.2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (9.6 mL, 63.6 mmol) in THF (35 mL) at −78 °C. The resulting red solution was stirred at −78 °C for 15 min, followed by the addition of selenium powder (1.67 g, 21.2 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 4 h under nitrogen. It was then oxidized by stirring under air for 12 h. The resulting brown solution was extracted with CH_2Cl_2 (50 mL × 3) and the combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by recrystallization from methanol afforded the optically active diselenide **1b** (9.80 g, 11.0 mmol, 52% yield): A yellow solid; mp 83–85 °C; $[\alpha]_D^{25}$ +40.45 (*c* 0.50, $CHCl_3$); ^{1}H

NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 6H), 0.12 (s, 6H), 0.90 (s, 18H), 3.82–3.87 (m, 2H), 4.07–4.10 (m, 2H), 4.43–4.48 (m, 2H), 5.64 (d, J = 0.49 Hz, 2H), 7.27–7.44 (m, 14H), 7.86–8.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.11, 18.4, 26.0, 65.1, 83.4, 125.47, 125.52, 125.6, 128.0, 128.6, 129.8, 130.5, 131.5, 133.6, 141.0, 163.4. HRMS *m/z* found: 893.2194, calcd for $C_{44}H_{57}N_2O_4Se_2Si_2$ M^+: 893.2199.

Preparation of Bis{2-[(4*S*,5*S*)-4-hydroxymethyl-5-phenyloxazolin-2-yl]phenyl} Diselenide (1c). Removal of *tert*-butyldimethylsilyl protecting group of **1b** (1.88 g, 2.10 mmol) was effected by stirring it with a solution of tetrabutylammonium fluoride (TBAF) (4.4 mL of 1.0 M THF solution, 4.4 mmol) in THF (20 mL) at room temperature for 8 h. The mixture was poured into saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (15 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The resulting oil was washed with hexane to remove the produced siloxane and the residue was purified by recrystallization from CH_2Cl_2/hexane to afford the corresponding diselenide **1c** (1.21 g, 1.83 mmol, 87% yield): A pale yellow solid; mp 99–101 °C; $[\alpha]_D^{25}$ +6.72 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (dd, J = 11.7, 3.9 Hz, 2H), 4.13 (dd, J = 11.7, 3.9 Hz), 4.47–4.51 (m, 2H), 5.57 (d, J = 7.32 Hz, 2H), 7.28–7.42 (m, 14H), 7.89–7.97 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.0, 76.9, 83.0, 125.7, 125.8, 125.9, 128.5, 128.9, 129.9, 130.6, 131.9, 133.7, 140.1, 164.4. HRMS *m/z* found: 665.0459, calcd for $C_{32}H_{28}N_2O_4Se_2$ M^+: 665.0465. Found: C, 57.28; H, 4.39; N, 3.73%. Calcd for $C_{32}H_{28}N_2O_4Se_2$: C, 58.01; H, 4.26; N, 4.23%.

X-ray Structural Analysis of 1c. Single crystals ($C_{32}H_{28}N_2O_4Se_2$) suitable for X-ray analysis were prepared by recrystallization from CH_2Cl_2/hexane. Diffraction data was collected on a Rigaku RAXIS-RAPID imaging plate area detector with Mo $K\alpha$ (λ = 0.71069 Å) radiation and a graphite monochromator at −100 °C. Details of the X-ray diffraction study are summarized in Table 2. For structure analysis and refinement, computations were performed using the CrystalStructure crystallographic software package.[20,21] Neutral atom scattering factors were taken from Ref. 22. Anomalous dispersion effects were included in F_{calc}[23]; the values of $\Delta f'$ and $\Delta f''$ were those of Ref. 24. The structure was solved by heavy-atom Patterson methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The weighting scheme $w = 1/\sigma^2(F_0)$ with $\sigma(F_0)$ from counting statistics gave satisfactory agreement analyses. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication and the deposition numbers CCDC-181729. The data are also deposited as Document No. 75041 at the Office of the Editor of Bull. Chem. Soc. Jpn.

General Procedure for Asymmetric Baeyer–Villiger Oxidation of 3-Phenylcyclobutanone (2a). A mixture of the diselenide **1b** (4.5 mg, 0.0050 mmol), $Yb(OTf)_3$ (6.2 mg, 0.010 mmol), pH 7.4 phosphate buffer solution (10 mL), 30% aqueous H_2O_2 solution (75 mL) and cyclododecane (as an internal standard; 50 mg) was stirred for 1 h in THF (0.50 mL) at room temperature under nitrogen. After cooling to 0 °C, a solution of 3-phenylcyclobutanone **2a** (73 mg, 0.50 mmol) in THF (0.50 mL) was added to the mixture and the resulting mixture was stirred for 24 h. It was then quenched with water (5 mL) and extracted with diethyl ether. The extract was dried over $MgSO_4$. The amount of the product **3a**[25] was determined by GLC analysis. For isolation of **3a**, the solvent was evaporated and the residue was purified by column chromatography using hexane/ethyl acetate = 5/1 as an eluent. The ee value of **3a** was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane/MeOH = 200/1, flow rate: 1.0 mL/min, column temperature: 30 °C, retention time: 54.2 min and 60.6 min).

Other lactones (**3b**,[26] **3c**,[27] **5**,[28] **7**,[29] and **9**[30]) were obtained from the corresponding ketones under similar reaction conditions.

Table 2. Summary of Crystallographic Data of **1c**

Empirical formula	$C_{32}H_{28}N_2O_4Se_2$
MW	662.50
Crystal syst	monoclinic
Space group	$P2_1$ (#4)
Cryst color	yellow
Lattice params	
a /Å	10.7364(6)
b /Å	9.1154(4)
c /Å	15.5693(8)
β /°	104.880(2)
V /Å^3	1472.6(1)
Z	2
D_{calc} /g cm^{-3}	1.494
μ(Mo $K\alpha$) /cm^{-1}	25.50
F(000)	668.00
Diffractometer	Rigaku RAXIS-RAPID
Radiation	Mo $K\alpha$ (λ = 0.71069 Å) graphite monochromated
Temp /°C	−100
Scan type	ω
Max. 2θ (°)	55.0
No. of rflns measd	3593
No. of observns ($I > 3.00\sigma(I)$)	2118
Structure soln	Patterson methods (DIRDIF99 PATTY)
Refinement	full-matrix least squares
No. of variables	395
Reflection/parameter ratio	5.36
Residuals: R ; R_w	0.037; 0.038
Goodness of fit (GOF)	0.10
Max shift/error in final cycle	0.16
Maximum peak in final Diff map /e Å^{-3}	0.55
Maximum peak in final Diff map /e Å^{-3}	−0.40

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