Catalytic Oxidation of Alcohols to Carbonyl Compounds Mediated by *N*-(Arylseleno)-4-chlorobenzenesulfonamide

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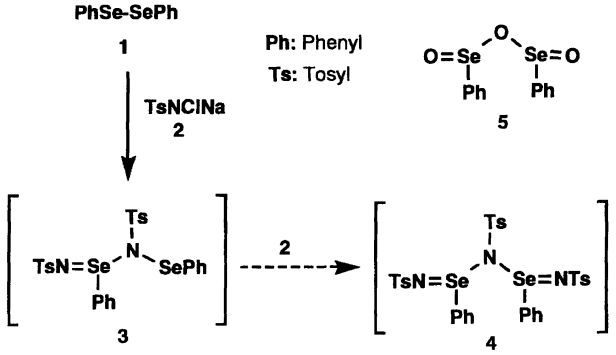
Most secondary alcohols and β,γ-unsaturated primary alcohols have been catalytically oxidized with *N*-chloro-4-chlorobenzenesulfonamide sodium salt to the corresponding carbonyl compounds by the addition of a 0.01—0.03 molar amount of dimethyl 2,2′-diselenodibenzoate in good-to-excellent yields, and a catalytic species, methyl 2-[*N*-(4-chlorophenylsulfonyl)aminoseleno]benzoate (**8**), was isolated from the reaction mixture. The catalytic oxidation cycle for this reaction is proposed; the decomposition of esters, which are produced by the reaction of alcohols with oxidized **8**, was found to be the rate-determining step.

Czarny has reported on the oxidation of amines to carbonyl compounds via imine intermediates by benzeneseleninic anhydride (**5**).[1] Since then, the oxidation of alcohols with organoselenium reagents has been extensively developed. Barton et al. have described the oxidation of alcohols to aldehydes and ketones using both benzeneseleninic anhydride (**5**) and benzeneseleninic acid.[2] Later, Kuwajima et al. described catalytic methods for the oxidation of alcohols using a 0.1—0.5 molar amount of a diaryl diselenide as the source of a catalyst and *t*-butylhydroperoxide as an oxidant.[3] These oxidations, except for the oxidation of amines, are due to the formation of an areneseleninate and/or an areneselenenate intermediate.[4]

The treatment of diphenyl diselenide (**1**) with 2 molar amounts of anhydrous chloramine-T (**2**) is supposed to give compound **3** (Scheme 1).[5] We expected that compound **3** might afford compound **4** upon further oxidation with chloramine-T. Compound **4** is a nitrogen analog of the aforementioned benzeneseleninic anhydride (**5**), and was expected to oxidize alcohols to carbonyl compounds. We therefore tried



Scheme 1.

to use diphenyl diselenide and chloramine-T to oxidize alcohols to carbonyl compounds, and finally found a highly efficient catalytic method which uses a catalytic amount of dimethyl 2,2′-diselenodibenzoate (**6**) and a stoichiometric amount of *N*-chloro-4-chlorobenzenesulfonamide sodium salt (**7**) as an oxidant. There are many catalytic methods for the oxidation of alcohols to carbonyl compounds; most of these reactions are catalyzed by transition-metal elements. However, the catalytic oxidation described here is a rare case which depends on a main group element (Se) as a redox catalytic center.

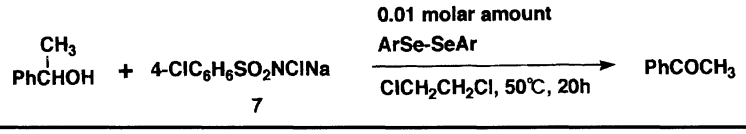
Results and Discussion

Although anhydrous chloramine-T (**2**) does not react with 2-octen-4-ol in 1,2-dichloroethane at 80 °C, the alcohol was oxidized to 2-octen-4-one in a yield of 48% when a 0.1 molar amount of diphenyl diselenide (**1**) was added to the reaction mixture. This result indicates that diphenyl diselenide served as a source of the oxidation catalyst, and encouraged us to find a better oxidant and a more efficient catalyst.

N-Chloro-4-chlorobenzenesulfonamide sodium salt (**7**) has an electron-withdrawing substituent (–Cl) on the para position of the benzene ring, and was expected to be a stronger oxidant than chloramine-T. When oxidant **7** was used for the catalytic oxidation of 2-octen-4-ol under the same condition as above, the yield of the ketone increased significantly to 70%. Although oxidant **7** is not commercially available, it is readily prepared from 4-chlorobenzenesulfonamide.[6] We therefore decided to use **7** instead of chloramine-T.

The variation in the diaryl diselenide (source of the catalyst) has been examined with *N*-chloro-4-chlorobenzenesulfonamide sodium salt (**7**) used as the oxidant and 1-phenylethanol as the substrate. The results are given in Table 1. Dimethyl 2,2′-diselenodibenzoate (Entry 2) and di-*t*-butyl 2,

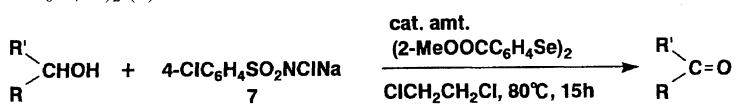
Table 1. Oxidation of 1-Phenylethanol by Using 4-$ClC_6H_4SO_2NClNa$ (**7**) and Catalytic Amount of Diaryl Diselenide



Entry	Diaryl diselenide	Yield / %[a]
1	$(C_6H_5Se)_2$ (**1**)	6.7
2	$(2\text{-}MeOOCC_6H_4Se)_2$ (**6**)	94.4
3	$(2\text{-}t\text{-}BuOOCC_6H_4Se)_2$	84.0
4	$(2\text{-}C_6H_5COC_6H_4Se)_2$	90.0
5	$(2\text{-}HOOCC_6H_4Se)_2$[b]	2.8
6	$(2\text{-}NO_2C_6H_4Se)_2$[7]	3.0
7	$(2\text{-}ClC_6H_4Se)_2$[8]	2.9
8	$(2,4,6,\text{-}Me_3C_6H_2Se)_2$[3c]	4.8
9	$(4\text{-}MeOOCC_6H_4Se)_2$[9]	4.1
10	$(4\text{-}ClC_6H_4Se)_2$[10]	1.1

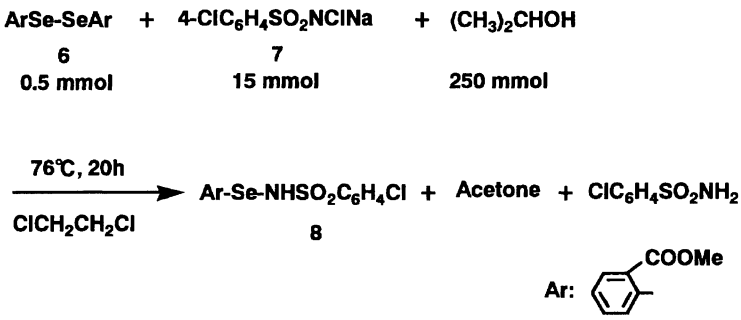
a) GC yield. The ratios of yield to conversion were in the range of 0.97—1.00. b) Sparingly soluble in the solvent.

Table 2. Oxidation of Alcohols by Using 4-$ClC_6H_4SO_2NClNa$ (**7**) and Catalytic Amount of $(2\text{-}MeOOCC_6H_4Se)_2$ (**6**)



Entry	Alcohol	Product	Molar amt. of **6**	Yield / %[a]
1	4-Octanol	4-Octanone	0.02	98
2	Cyclododecanol	Cyclododecanone	0.02	99 (98)[b]
3	Cyclohexanol	Cyclohexanone	0.03	96
4	2-Cyclohexenol	2-Cyclohexenone	0.01	99
5	(*E*)-2-Octen-4-ol	(*E*)-2-Octen-4-one[c]	0.02	98 (86)[b]
6	1-Phenylethanol	Acetophenone	0.01	99
7	5-Decyn-4-ol	5-Decyn-4-one	0.01	100
8	6-Methyl-5-hepten-2-ol	6-Methyl-5-hepten-2-one	0.02	6[d]
9	Benzyl alcohol[e]	Benzaldehyde	0.01	89
10	Geraniol	Geranial[f]	0.02	78
11	1-Decanol	Decanal[g]	0.02	7[g]

a) GC yield on 0.25 mmol reactions unless otherwise noted. b) Isolated yield on 10 mmol scale. c) Only *E* isomer was detected. d) The unreacted alcohol was recovered (87%). e) Reaction temperature: 50 °C. f) Neral (*Z* isomer) was formed in a yield of 1.8%. g) The unreacted alcohol was recovered (42%). When 0.16 molar amount of **6** was used, the yield was 93%.



Scheme 2.

2′-diselenodibenzoate (Entry 3), each of which has an ester group at the ortho position of the benzene ring, are 13—14 times more active than diphenyl diselenide (Entry 1) as sources of the catalyst. However, the *p*-methoxycarbonyl-substituted reagent (Entry 9) is much less active than the corresponding ortho-substituted reagent (Entry 2), and shows even less activity than diphenyl diselenide (**1**). This implies that the increase in the activity is not due to an inductive ef-

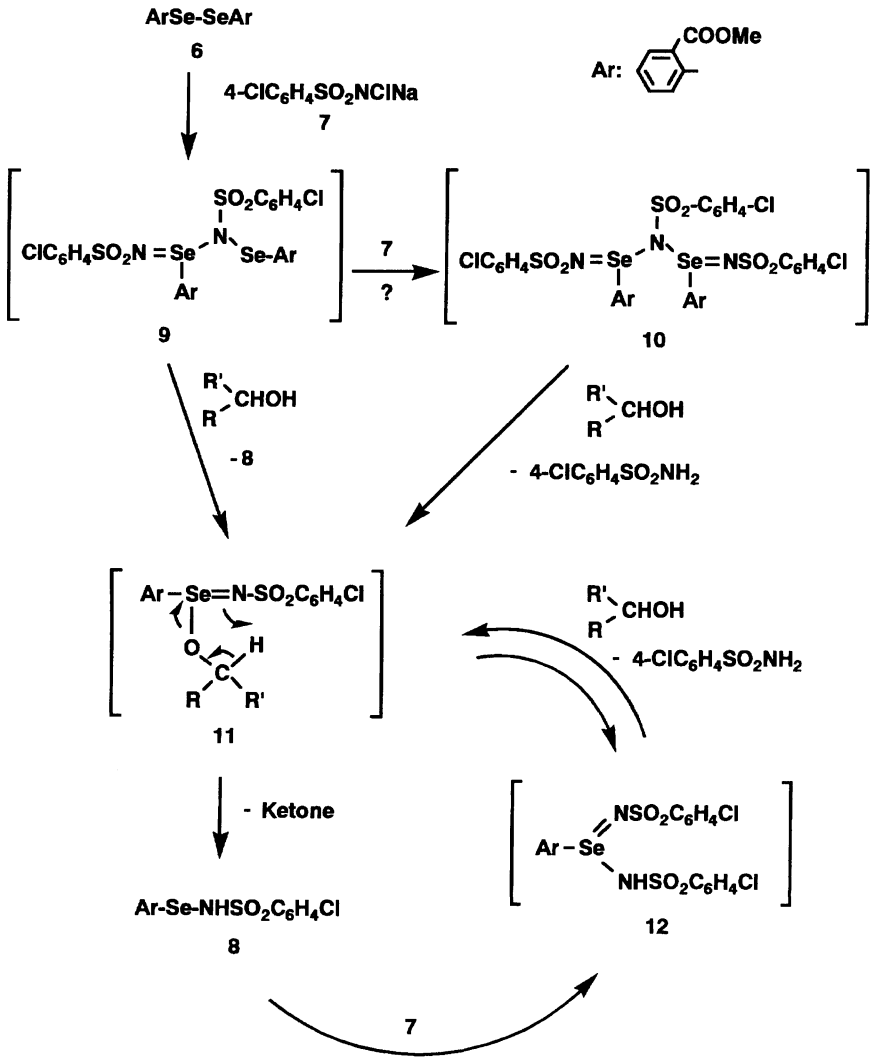


Fig. 1. Mechanism of the catalytic oxidation of alcohols.

fect of the ester groups on the benzene ring. The *o*-benzoyl-substituted reagent (Entry 4) also showed almost the same activity as the *o*-methoxycarbonyl-substituted reagent (Entry 2).[11]

Since the *o*-methoxycarbonyl-substituted reagent **6** was the most active among the diaryl diselenides examined, and is easily prepared, it was selected as a source of the catalyst. Table 2 shows the results of the oxidation of various alcohols when a catalytic amount of the diselenide **6** and a stoichiometric amount of oxidant **7** were used. Saturated secondary alcohols (Entries 1—3) and β,γ-unsaturated secondary alcohols (Entries 4—7) were oxidized to ketones in high yield using a 0.01—0.03 molar amount of the diselenide **6**. However, a secondary alcohol with an isolated double bond (Entry 8) was reluctant, and the reaction ceased at 13% conversion. Although β,γ-unsaturated primary alcohols could be oxidized to the corresponding α,β-unsaturated aldehydes in good yields (Entries 9 and 10), the oxidation of a saturated primary alcohol under similar conditions resulted in the formation of the corresponding aldehyde in poor yield (Entry 11). This is attributed to a further oxidation of the aldehyde to the corresponding carboxylic acid.

In order to isolate an actual catalyst, the reaction shown in Scheme 2 was performed in the presence of a large excess of 2-propanol relative to oxidant **7**, and the divalent selenium compound **8** was isolated from the reaction mixture. Compound **8** did not oxidize 2-propanol, but catalyzed the oxidation of the alcohol when combined with oxidant **7**. Therefore, **8** is considered to be a catalytic species in the catalytic cycle and a precursor of the active form of the oxidant.

A mechanism which accounts for the catalytic oxidation of alcohols is proposed in Fig. 1. First, dimethyl 2,2′-diselenodibenzoate (**6**) is oxidized to **9** with 2 molar amounts of *N*-chloro-4-chlorobenzenesulfonamide sodium salt (**7**),[5] and a part of **9** may be oxidized further to **10** with a 1 molar amount of oxidant **7**. A nucleophilic attack of an alcohol to **9** and/or **10** would afford ester **11**, which enters the catalytic oxidation cycle. The decomposition of the ester **11** would afford a ketone and a divalent selenium compound **8**, which is the catalytic species and is oxidized with oxidant **7** to give a tetravalent selenium compound **12**. There is a possibility of the formation of areneselenenate esters (ArSe–O–R) by the reaction of compound **8** with alcohols. The selenenate

esters would then decompose to carbonyl compounds,[3c] or would be oxidized to **11** with oxidant **7**. However, such a possibility is ruled out, because the alcohols (1-phenylethanol and diphenylmethanol) did not react with **8** (in the absence of oxidant **7**), and were completely recovered.[12] Compound **12** is the actual oxidizing species, and would react with the alcohol to form the intermediate **11** in the catalytic oxidation cycle.

It was difficult to oxidize the alcohol with an isolated double bond (see above). This was presumably due to trapping of catalyst **8** and/or its precursor **9** by the isolated double bond of the alcohol. The ionic addition of divalent selenium compounds has been well studied, and the addition of N^1-(arylseleno)areneseleninamidines, such as **9**, to olefins has been reported.[5]

The catalytic oxidation cycle shown in Fig. 1 comprises three steps (**11**→**8**, **8**→**12**, and **12**→**11**). The step **12**→**11** is reversible, because the reaction rate is retarded by the addition of 4-chlorobenzenesulfonamide. In order to examine whether the decomposition of the ester **11** is a rate-determining step, the oxidation rates of 1-phenylethanol and 1-phenylethanol-1-*d* were measured, and the ratio of the rates for the former and latter was 5.2 at 60 °C. Such a large isotope effect indicates that the proton-transfer step in the decomposition of the ester (**11**→**8**) is rate-determining.[13]

Experimental

The melting points were determined on a capillary-tube melting-point apparatus and are uncorrected. The infrared (IR) spectra were recorded on a JASCO FT/IR 5000 infrared spectrometer, and the proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on JEOL FX-90Q or JEOL JNM-EX270 spectrometers. Tetramethylsilane (TMS) was used as an internal standard; the chemical shifts are denoted in ppm downfield to TMS. Gas chromatographic (GC) analyses were performed on a Hitachi 163 equipped with glass columns (3 mm i.d.) or a HP 5890 equipped with a capillary column. 1,2-Dichloroethane was dried and stored over molecular shieves 3A.

***N*-Chloro-4-chlorobenzenesulfonamide Sodium Salt (7).** *N*-Chloro-4-chlorobenzenesulfonamide sodium salt monohydrate (49.7 g) was prepared according to the reported method,[6] and dried over P_2O_5 at 85 °C in vacuo for 2 h to give anhydrous *N*-chloro-4-chlorobenzenesulfonamide sodium salt.

Dimethyl 2,2′-Diselenodibenzoate (6). 2,2′-Diselenodibenzoic acid was prepared according to the reported method,[15] and methylated with diazomethane (diethyl ether solution) to give dimethyl 2,2′-diselenodibenzoate: Mp 142—143 °C (lit,[16] mp 143—144 °C); IR (KBr) 1691 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 4.01 (6H, s, OMe), 7.20—8.08 (8H, aromatic).

Di-*t*-butyl 2,2′-Diselenodibenzoate. Liquid 2-methylpropene (ca. 2 mL) was added to a cooled solution (ca. −20 °C) of 2,2′-diselenodibenzoic acid (400 mg, 1 mmol) in a mixture of 0.1 mL of concd H_2SO_4 and 4 mL of 1,2-dimethoxyethane in a pressure bottle,[17] and the mixture was shaken for 100 h at room temperature. After the addition of cold water, the reaction mixture was extracted with diethyl ether (10 mL×2). The combined extracts were washed with sat. $NaHCO_3$, brine, dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by preparative silica-gel TLC and recrystallized from hexane to give 23 mg (9%) of di-*t*-butyl 2,2′-diselenodibenzoate: Mp 161.5—162.5 °C; IR (KBr) 1668 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 1.63 (18H, s, *t*-butyl), 6.90—8.05 (8H, aromatic). Found: C, 51.34; H, 5.32%. Calcd for $C_{22}H_{26}O_4Se_2$: C, 51.57; H, 5.11%.

Bis(2-benzoylphenyl) Diselenide. To an ice-cooled, stirred solution of 292 mg (1 mmol) of 2-benzoylbenzeneseleninic acid[18] in 5 mL of MeOH were added 0.5 mL of 2 M HCl and 1.7 mL of 10% $NaHSO_3$ solution, successively. After standing overnight at room temperature, the precipitated solid was collected by filtration, washed with water, dried and crystallized from EtOAc/hexane to give 161 mg (64%) of bis(2-benzoylphenyl) diselenide: Mp 116.5—117.5 °C (lit,[18] 116.5—117.5 °C); IR (KBr) 1636 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ = 7.15—8.05 (18H, aromatic).

General Procedure Used for the Determination of Yields in the Catalytic Oxidation of Alcohols. To a mixture of alcohol (1 mmol) to be oxidized and one of the diaryl diselenides (Table 1, 0.01—0.03 mmol) in 4 mL of 1,2-dichloroethane was added 1.2 mmol of the oxidant (anhydrous chloramine-T[19] or anhydrous *N*-chloro-4-chlorobenzenesulfonamide sodium salt); the mixture was magnetically stirred and heated at 80 °C under a nitrogen atmosphere for 12 h. A suitably chosen straight chain hydrocarbon was added as an internal standard for a GC analysis to the cooled reaction mixture; the resulting mixture was then diluted with 8 mL of diethyl ether and 2 mL of aqueous 1 M NaOH (M = mol dm^{-3}). After stirring for 1 min, the organic layer was separated, dried ($MgSO_4$), and analyzed by GC.

Large-Scale Oxidation of Alcohols with *N*-Chloro-4-chlorobenzenesulfonamide Sodium Salt (7) and Catalytic Amounts of Dimethyl 2,2′-Diselenodibenzoate (6). The preparation of cyclododecanone is representative: To a mixture of 18.4 g (100 mmol) of cyclododecanol and 0.97 g (2 mmol) of dimethyl 2,2′-diselenodibenzoate in 300 mL of 1,2-dichloroethane was added 27.4 g (110 mmol) of anhydrous *N*-chloro-4-chlorobenzenesulfonamide sodium salt; the mixture was refluxed under a nitrogen atmosphere for 15 h. Most of the solvent (ca. 250 mL) was then removed on a rotary evaporator. Diethyl ether (400 mL) was added and the resulting mixture was washed successively with 100 mL portions of aqueous 1 M NaOH, water, and brine. After separating the ether layer, the ethereal solution was dried over $MgSO_4$ and concentrated on a rotary evaporator; the resulting solid was distilled under a vacuum (85 °C, 133 Pa) to give 17.9 g (98%) of cyclododecanone: Mp 58—61 °C (lit,[20] mp 59—61 °C).

Instability of Decanal to Oxidant 7. A mixture of decanal (78 mg, 0.50 mmol), *N*-chloro-4-chlorobenzenesulfonamide sodium salt (130 mg, 0.52 mmol), and tridecane (internal standard for GC analysis, 20 mg) in 3 mL of 1,2-dichloroethane was stirred at 80 °C under a nitrogen atmosphere for 15 h. The reaction mixture was poured into 10 mL of diethyl ether, and washed with a solution consisting of 1 mL of brine and 0.2 mL of concd HCl. The separated organic layer was analyzed by GC (0.53 mm i.d. 15 m DB-1; 110→200 °C, 15 °C min^{-1}; flow rate 12 mL min^{-1}). A GC analysis showed the yields of the remaining aldehyde and decanoic acid to be 28 and 59%, respectively.

The Isolation of Methyl 2-[*N*-(4-Chlorophenylsulfonyl)aminoseleno]benzoate (8). To a mixture of 15.03 g (250 mmol) of 2-propanol and 0.214 g (0.5 mmol) of dimethyl 2,2′-diselenodibenzoate in 50 mL of 1,2-dichloroethane was added 3.72 g (15 mmol) of anhydrous *N*-chloro-4-chlorobenzenesulfonamide sodium salt. After heating at 76 °C for 20 h under a nitrogen atmosphere, the precipitated solid (NaCl) was filtered off and the filtrate was concentrated to dryness. The residual solid was extracted with $CHCl_3$, and the combined extracts were concentrated and chromatographed

on silica gel using 1 : 4 EtOAc/hexane to give 0.234 g (58%) of **8** as an oil. An analytical sample was obtained by preparative HPLC (LiChrosorb RP-18, 4 : 1 MeOH/H_2O): IR (neat) 3270 (NH), 1668 (C=O), 1325, 1162 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.97 (3H, s, OMe), 5.62 (1H, s, NH), 7.26—8.03 (8H, aromatic). Found: C, 41.42; H, 3.23; N, 3.73%. Calcd for $C_{14}H_{12}ClNO_4SSe$: C, 41.55; H, 2.99; N, 3.46%.

Attempted Reaction of Alcohols with Compound 8. A solution of 1-phenylethanol (61 mg, 0.5 mmol), compound **8** (20 mg, 0.05 mmol), and heptadecane (23 mg, an internal standard for GC analysis) in 3 mL of 1,2-dichloroethane was heated at 80 °C for 5 h under a nitrogen atmosphere. A GC analysis (1 m 15% DEGS on 80/100 mesh Uniport B; 105 °C; flow rate 40 mL min^{-1}) showed that 100% of the starting alcohol remained.

The reaction of diphenylmethanol with compound **8** was similarly attempted. A GC analysis showed that 100% of the starting alcohol remained, and no benzophenone was detected

1-Phenylethanol-1-*d*. To a stirred solution of 4 g (33.29 mmol) of acetophenone in 50 mL of ethanol was added 418 mg (41.5 mmol) of $NaBD_4$ (98 atom % D, Aldrich) by portions. The reaction mixture was stirred for 17 h at room temperature, and then heated at 60 °C for 1 h. About 100 mL of a 10% NaCl solution was added after cooling, and the resulting solution was extracted with five 50-mL portions of diethyl ether. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by Kugelrohr distillation (110 °C, 2000 Pa) to give 3.748 g (91.4%) of 1-phenylethanol-1-*d* containing 2.1% of 1-phenylethanol: ^1H NMR ($CDCl_3$) δ = 1.49 (3H, s, methyl), 1.85 (1H, s, OH), 4.89 (0.021H, q, J = 6.6 Hz, benzyl proton of 1-phenylethanol), 7.34—7.39 (5H, m, aromatic).

Rate Comparison. Solutions of dimethyl 2,2′-diselenodibenzoate (8.6 mg, 0.02 mmol) and heptadecane (32 mg, internal standard for GC analysis) in 1,2-dichloroethane (12 mL) were placed in two reaction vessels under a nitrogen atmosphere. After addition of anhydrous *N*-chloro-4-chlorobenzenesulfonamide sodium salt (595 mg, 2.4 mmol), the mixtures were stirred magnetically at room temperature for 15 min, and then heated at 60±0.2 °C using a temperature-controlled bath. The oxidation reactions were initiated by the addition of 1-phenylethanol (244 mg, 2 mmol) and 1-phenylethanol-1-*d* (246 mg, 2 mmol), respectively. Samples of 5 μL were withdrawn periodically, diluted with 0.2 mL of diethyl ether, washed with aqueous 1 M NaOH, and analyzed by GC (1 m 15% DEGS on 80/100 mesh Uniport B, 105 °C, flow rate 40 mL min^{-1}). The amounts of the ketone produced were plotted against the reaction times, and the initial reaction rates of the oxidation of 1-phenylethanol and 1-phenylethanol-1-*d* were determined by the differentiation of fitted equations of the third degree in the reaction time.[21] The observed reaction rates (d[ketone]/dt) at time 0 for 1-phenylethanol and 1-phenylethanol-1-*d* (contains 2.1% of the non-deuterated alcohol) were, respectively, 5.88×10^{-4} and 1.23×10^{-4} M min^{-1}, which give k_H/k_D = 5.2 by considering the percentage of the non-deuterated alcohol.

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11) The selenium atom in the putative intermediate **11** (Fig. 1) could be trigonal bipyramidal rather than pyramidal due to the coordination of the carbonyl oxygen to the selenium atom in the ortho position.[14] The intermediate **11** would consequently decompose faster since the imino nitrogen atom is closer to the leaving hydrogen atom in the trigonal bipyramid than in the pyramid. This may be the reason why diaryl diselenides with *o*-carbonyl groups are good catalyst sources. A nitro group also can coordinate to the selenium atom.[14] However, the activity of bis(2-nitrophenyl) diselenide is low (Entry 6, Table 1). The reason for this is not clear, but this may be because the nitro group is powerfully electron-attracting, and the positively polarized selenium atom would resist to the oxidation by oxidant **7**.

12) If the selenenate ester was formed by the reaction of **8** with diphenylmethanol, it could decompose to benzophenone, and hence the alcohol could not be recovered completely. See Ref. 3c.

13) The ratio more than 2 suggests that the proton transfer occurs in the transition state of the rate-determining step. See: C. Walsh "Enzymatic Reaction Mechanisms," W. H. Freemann and Co., New York (1979), p. 113.

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