Electroreductive Deoxygenation of Methanesulfonates of α-Hydroxy Esters via a Catalytic Selenation–Deselenation Sequence

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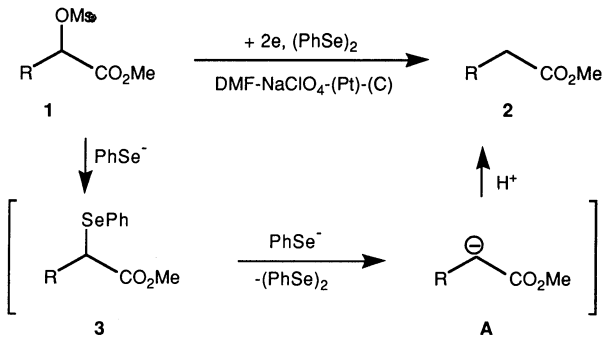
Synopsis. The methanesulfonates of α-hydroxy esters were converted to the corresponding deoxygenated esters in 70—88% yields by the indirect electrolysis with diphenyl diselenide as a recyclable reagent in a divided cell. This deoxygenation method may involve the formation of α-phenylselenoester by replacement of α-methylsulfonyloxyl group with phenylselenide anion followed by capture of the α-phenylseleno group with phenylselenide anion.

Reduction of α-hydroxyl function to make a methylene group is an important procedure particularly in the field of carbohydrates and steroids.[1] Deoxygenations of alcohols via homolytic cleavage of a C–O bond are accomplished by treating the corresponding *O*-thioesters with trialkyltin hydride (Barton–McCombie reaction),[2] alkali metal,[3] or irradiation.[3] Direct electroreduction of the methanesulfonates[4] is also effective for this purpose. Hydroxyl groups attached α to the ester function can be smoothly eliminated by the reaction with SmI_2[5] and others.[6] However, development of a catalytic deoxygenation method by use of recyclable reagent is desirable. Recently, we have investigated the reductive transformation of epoxy carbonyl compounds to the corresponding β-hydroxy derivatives by using a catalytic amount of diphenyl diselenide or ditelluride in an indirect electrolysis system.[7] In this paper, we report an extension of this method to a cleavage of the carbon–oxygen bond of the methanesulfonates **1** derived from α-hydroxy esters, giving the ester **2**.[8]



Scheme 1.

The electrolysis of the methanesulfonate **1a** was carried out in a DMF solution containing $NaClO_4$ as an electrolyte with (Pt)–(C) electrode system. To the catholyte, malonic ester was added as a proton source and 0.25 equivalent of diphenyl diselenide was employed as a mediator. When 4.2 F mol^{-1} of electricity had been charged, the corresponding ester **2a** was produced in a yield of 83% together with quantitatively recovered diphenyl diselenide.

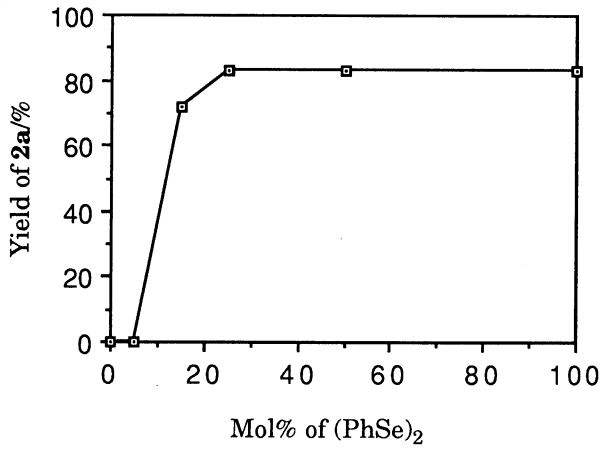


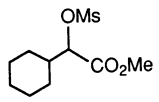
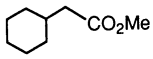
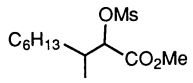
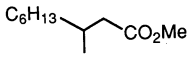
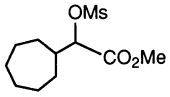
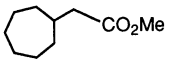
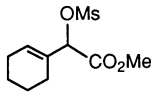
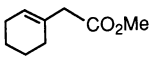
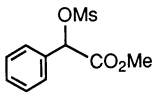
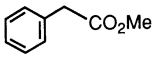
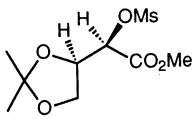
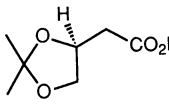
Fig. 1. Yield of **2a** under various amount of $(PhSe)_2$.

The correlation of the yield of the compound **2a** under various amount of diphenyl diselenide is shown in Fig. 1. Decreasing the amount of diphenyl diselenide from one equivalent to 0.25 equivalent, the desired compound **2a** is given in a yield of over 80%. Even with 0.15 equivalent of diphenyl diselenide, the compound **2a** is obtainable in 72% yield. However, decreasing the amount of diphenyl diselenide less than 0.15 equivalent, the compound **2a** can not be produced at all.[9] Therefore, the addition of more than 0.15 equivalent of diphenyl diselenide is desirable for the smooth conversion.

The electroreduction of α-methylsulfonyloxy esters is considered to proceed through an ionic mechanism. In the first step, the methylsulfonyloxyl group of **1** is replaced with phenylseleno group, giving the selenide **3**. In the second step, phenyl selenide anion attacks a phenylseleno group on α position of **3** to yield the corresponding anionic species **A** and diphenyl diselenide (Scheme 1). The desired ester would be produced by protonation of the enolate.[7] In this respect, electrochemical deselenation of **3** was examined. Thus, electroreduction of **3a**, separately prepared from **1a** by reaction with selenium borate complex, $PhSeB(OEt)_3$,[10] in the presence of a catalytic amount of diphenyl diselende, resulted in clean removal of α-phenylseleno group of **3a**, giving **1a** in 84% yield.

We examined to apply the deoxygenation method to various substrates under above conditions and the results are shown in Table 1. In all cases, the α-methylsulfonyloxy esters **1** are converted to the corresponding esters **2** in good yields. The conditions are compatible with the substrates bearing olefin and acetal moieties (Entries 4 and 6).

Table 1. Indirect Electroreduction of the Methanesulfonates **1** by Using $(PhSe)_2$ as a Mediator[a)]

Entry	Substrate	Electricity / F mol^{-1}	Product	(Yield/%)[b)]
1	 **1a**	4.2	 **2a**	(83)
2	 **1b**	5.1	 **2a**	(70)
3	 **1c**	4.9	 **2c**	(85)
4	 **1d**	4.4	 **2d**	(88)
5	 **1e**	4.5	 **2e**	(72)
6	 **1f**	5.0	 **2f**	(82)

a) Substrates (1 mmol) were electrolyzed in the presence of $(PhSe)_2$ (0.25 mmol), and $CH_2(CO_2Et)_2$ (5 mmol) in a DMF–$NaClO_4$ (0.5 M)–(Pt)–(C) system at 50 °C. b) Yields based on isolated products.

Experimental

Apparatus and Procedures. Boiling points indicated by an air-bath temperature are uncorrected. IR spectra were recorded on a JASCO FT-8000 spectrometers. ^{1}H NMR spectra were taken in $CDCl_3$ (Me_4Si as a standard) on a Varian VXR-200 instrument. Column chromatographies were carried out with a Merck Kieselgel 60, Art. 7734 (silica gel) with hexane–AcOEt as an eluent. Starting materials **1** were prepared by methylsulfonylation of α-hydroxy esters.[8)] An H-type cell (40 ml volume) with a Nafion® (NO. 324) diaphragm was used. The cathodic compartment was fitted with a thermometer, a magnetic stirring bar, and an argon inlet glass tube. A glassy carbon (3×1 cm^2) as a cathode and a platinum foil (2×1 cm^2) as an anode were immersed parallel to each other 4 cm apart.

Indirect Electroreduction of the Methansulfonate 1a with $(PhSe)_2$ as a Mediator. Typical Procedure: A mixture of **1a** (250 mg, 1 mmol), diethyl malonate (800 mg, 5 mmol), and diphenyl diselenide (78 mg, 0.25 mmol) was dissolved in a 0.5 M (1 M=1 mol dm^{-3}) $NaClO_4$–DMF solution (8 ml) and charged in the cathodic compartment of a divided cell. To the anodic compartment was added a 0.5 M $NaClO_4$–DMF solution (8 ml). A glassy carbon plate as a cathode and a platinum foil as an anode were immersed in the electrolyte solution. Prior to the electrolysis, the catholyte was bubbled with argon for 30 min and the entire mixture was electrolyzed at 50 °C under a constant applied voltage of 5 V. The electrolysis was interrupted when 4.2 F mol^{-1} of electricity (1 F=96480 C) had been passed (it required 7.3 h). The catholyte was bubbled with air for 10 min, and then diluted with hexane–ether (1 : 1), and the mixture was poured into aqueous 10% tartaric acid (10 ml) in a separatory funnel. The organic layer was separated and extracted with hexane–ether (1 : 1, 15 ml×4). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (40 ml×2), and brine (40 ml), dried over sodium sulfate, and concentrated on a rotary evaporator. Column chromatography (SiO_2) of the residue gave 126 mg (81%) of **2a** and 78 mg (100%) of $(PhSe)_2$. Spectral data of the compounds listed in Table 1 are as follows.

Methyl Cyclohexaneacetate (2a): Bp 43 °C/1 Torr (1 Torr= 133.322 Pa); IR (film) 1742, 1464, 1274, 1123, 1073 cm^{-1}; ^{1}H NMR (200 MHz) δ=0.82—1.10 (m, 2H, CH_2), 1.15—1.40 (m, 3H, CH, CH_2), 1.57—1.88 (m, 6H, CH_2), 2.17 (d, J=7.0 Hz, 2H, CH_2CO), 3.64 (s, 3H, OCH_3); ^{13}C NMR (50 MHz) δ=25.0, 26.1, 33.0, 34.9, 41.9, 51.3, 173.6.

Methyl 3-Methylnonanote (2b): Bp 52 °C/1 Torr; IR (film) 1742, 1462, 1437, 1201, 1170, 1011, 917, 735 cm^{-1}; ^{1}H NMR (200 MHz) δ=0.87 (t, J=6.6 Hz, 3H, CH_3), 0.91 (d, J=6.5 Hz, 3H, CH_3), 1.26 (brs, 10H, CH_2), 1.93 (m, 1H, CH), 2.10 (dd, J=14.5, 8.0 Hz, 1H, CHCO), 2.26 (dd, J=14.5, 5.9 Hz, 1H, CHCO), 3.66 (s, 3H, OCH_3); ^{13}C NMR (50 MHz) δ=14.0, 19.7, 22.6, 26.8, 29.4, 30.3, 31.8, 36.7, 41.6, 51.3, 173.8.

Methyl Cycloheptaneacetate (2c): Bp 47 °C/1 Torr; IR (film) 1742, 1462, 1437, 1255, 1195, 1149, 1038 cm^{-1}; ^{1}H NMR (200 MHz) δ=1.10—1.28 (m, 2H, CH_2), 1.35—1.76 (m, 10H, CH_2), 1.88—2.08 (m, 1H, CH), 2.21 (d, J=7.3 Hz, 2H, CH_2CO), 3.64 (s, 3H, OCH_3); ^{13}C NMR (50 MHz) δ=26.2, 28.2, 34.5, 36.4, 42.5, 51.3, 173.7.

Methyl 1-Cyclohexene-1-acetate (2d): Bp 45 °C/1 Torr; IR (film) 1742, 1671,1437, 1334, 1299, 1156, 1131, 1017, 922 cm^{-1}; ^{1}H NMR (200 MHz) δ=1.48—1.72 (m, 4H, CH_2), 1.97—2.07 (m, 4H, CH_2), 2.93 (s, 2H, CH_2CO), 3.65 (s, 3H, OCH_3), 5.54 (m, 1H, C=CH); ^{13}C NMR (50 MHz) δ=21.9, 22.7, 25.3, 28.3, 43.4, 51.6, 125.7, 131.4, 172.4.

Methyl (*R*)-2,2-Dimethyl-1,3-dioxolane-4-acetate (2f): $[\alpha]_D^{20}$ −16.2° (*c* 1.02, $CHCl_3$) (lit,[6)] −16.7°); bp 51—52 °C/1 Torr; IR (film) 1742, 1216, 1114, 1067, 839 cm^{-1}; ^{1}H NMR (200 MHz) δ=1.35 (s, 6H, CH_3), 2.48 (dd, J=15.9, 6.4 Hz, 1H, CHCO), 2.68 (dd, J=15.9, 6.5 Hz, 1H, CHCO), 3.61 (dd, J=8.3, 6.3 Hz, 1H, OCH), 3.66 (s, 3H, OCH_3), 4.12 (dd, J=8.3, 6.0 Hz, 1H, OCH), 4.43 (m, 1H, OCH); ^{13}C NMR (50 MHz) δ=25.4, 26.8, 38.7, 51.7, 69.0, 72.0, 109.2, 170.9.

Preparation of Methyl Cyclohexane(2-phenylseleno)acetate (3a). To a solution of $NaBH_4$ (83 mg, 2.2 mmol) in EtOH (3 ml) was added diphenyl diselenide (312 mg, 1.0 mmol) in EtOH (1 ml) at 0 °C. After being stirred for 1 h at room temperature, was added **1a** (500 mg, 2.0 mmol) in EtOH (1 ml) to the above solution at 0 °C and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with aqueous 10% NH_4Cl and the products were extracted with AcOEt. Extract was washed with brine and the crude oil was purified by column chromatography (SiO_2, hexane–AcOEt 10 : 1) to give 344 mg (55%) of **3a** as an oil: IR (film) 1734 (COO), 1578, 1479, 1437, 1288, 1249, 1137, 909 cm^{-1}; ^{1}H NMR (200 MHz) δ=0.87—1.37 (m, 5H, CH_2), 1.55—1.88 (m, 5H, CH_2), 2.12—2.25 (m, 1H, CH), 3.43 (d, J=9.7 Hz, 2H, CHCO), 3.58 (s, 3H, OCH_3), 7.20—7.32 (m, 3H, ArH), 7.52—7.63 (m, 2H, ArH); ^{13}C NMR (50 MHz) δ=25.87, 25.94, 26.1, 31.4, 31.5, 39.3, 51.8, 52.0, 128.2, 128.7, 129.0, 135.3, 173.0.

Deselenation of 3a to 2a by Indirect Electroreduction with $(PhSe)_2$. Similar indirect electroreduction of **3a** (311 mg, 1.0 mmol) as above with $(PhSe)_2$ (78 mg, 0.25 mmol) in a

0.5 M $NaClO_4$–DMF solution (8 ml) in the cathodic chamber gave 131 mg (84%) of **2a**. In this operation 209 mg of diphenyl diselenide was recovered.

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