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Electroreductive Ring-Opening of α,β-Epoxy Carbonyl Compounds and Their Homologues through Recyclable Use of Diphenyl Diselenide or Diphenyl Ditelluride as a Mediator

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A novel access to β-hydroxy carbonyl compounds from the corresponding α,β-epoxy carbonyl compounds has been attained through the recyclable use of diphenyl diselenide or diphenyl ditelluride as an electroreduction mediator in a $MeOH–NaClO_4$–(Pt) system. α,β-Epoxy ketones are converted to the corresponding aldols in the presence of malonic esters. Similarly, α,β-epoxy esters and nitriles can be reduced to the corresponding β-hydroxy compounds in the presence of acetic acid.

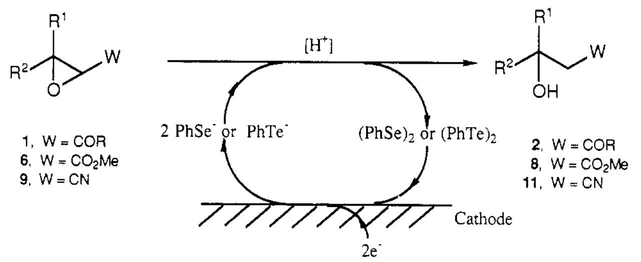
The formation of alkenes and allylic alcohols via syn elimination of organoselenium derivatives has previously been achieved through the consumption of at least 1 equiv of a selenating reagent.[1] A recent upsurge of interest in the recyclable use of selenium and tellurium reagents, however, has led to the development of their catalytic use, as exemplified in the conversion of amines to amides[2] and in the reductive decarbonylation of aromatic ketones.[3] We have also reported the catalytic use of diphenyl diselenide in the conversion of alkenes to 3-alkoxyalkenes through electrooxidation.[4]

Although phenyl selenide and telluride anions generated by the electroreduction of diselenides and ditellurides[5a,b] have been exploited in selenation and telluration reactions through either direct replacement[6] or an $S_{RN}1$ mechanism,[5] the recyclability of these electrogenerated anionic species has never been established. We describe herein the following electrogenerated mediator-assisted ring-opening reactions of epoxy compounds: (1) the conversion of α,β-epoxy ketones to β-hydroxy ketones (aldol synthesis) and (2) the conversion of α,β-epoxy esters and nitriles to the corresponding β-hydroxy esters and nitriles (Scheme I).

Results and Discussion

Electroreductive Cleavage of α,β-Epoxy Ketones. A variety of reagents have been used for the reductive cleavage of a carbon–oxygen bond at the α position of α,β-epoxy ketones to generate β-hydroxy ketones (aldols).[7]

Scheme I[a]



[a] $[H^+]$ = dimethyl malonate or acetic acid.

Table I. Effect of a Solvent–Electrolyte–(Electrode) System on the Indirect Electroreduction of Isophorone Oxide (1a)[a]

entry	solvent	electrolyte	cathode	yield of **2a**,[b] %
1	MeOH	$NaClO_4$	Pt	86
2	MeOH	$NaClO_4$	C	35
3	MeOH	$NaClO_4$	Pb	21
4	MeOH	$LiClO_4$	Pt	75
5	MeOH	Bu_4NClO_4	Pt	41
6	EtOH	$NaClO_4$	Pt	76
7	$THF–H_2O$ = 9:1	$NaClO_4$	Pt	43
8	DMF	$NaClO_4$	Pt	32

[a] Carried out with **1a** (1 mmol), $(PhSe)_2$ (1 mmol), and dimethyl malonate (5 mmol) under an applied voltage of 3 V in a 0.1 M solution of the electrolyte (10 mL) by passing 3.5 F/mol of electricity through a divided cell. [b] Based on isolated products.

The direct electroreduction of steroidal epoxy ketones has also been examined, but these reactions provide the desired aldols in ca. 30% yields, along with byproducts derived through simultaneous dehydration and pinacolization.[8,9]

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Table II. Effect of a Solvent–Electrolyte–Electrode System and Proton Source in the Direct Electroreduction of 1a[a]

entry	solvent–electrolyte system[b]	cathode material	proton source	electricity, F/mol	product, yield,[c] %		
					2a	**3a**	**4a + 5a**
1	A	(C)	–	2.5	trace	–	37
2	A	(C)	$CH_2(CO_2Et)_2$	6.3	65	trace	–
3	B	(C)	$CH_2(CO_2Et)_2$	7.0	63	trace	–
4	B	(C)	C_6H_5OH	5.0	11	13	–
5	B	(Pb)	$CH_2(CO_2Et)_2$	4.0	6	24	–

[a] Carried out by using **1a** (1 mmol) at 12 mA/cm^2 in a divided cell under Ar. [b] System A: THF–H_2O(9:1)–Bu_4NBF_4(0.1 M). System B: DMF–Et_4NOTs(0.5 M). [c] Based on isolated products.

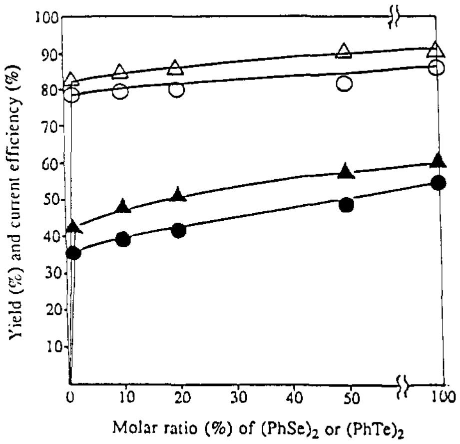


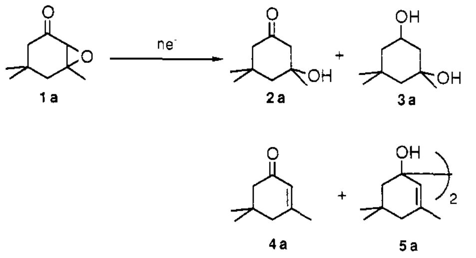
Figure 1. Yields and current efficiencies of **2a** vs $(PhSe)_2$ or $(PhTe)_2$. Symbols of yield and current efficiency of **2a** with $(PhSe)_2$: ○, ●. Symbols of yield and current efficiency of **2a** with $(PhTe)_2$: △, ▲.

The development of a sufficiently catalytic procedure for obtaining β-hydroxy carbonyl compounds has thus become a priority among synthetic chemists.[10]

The electroreductive ring-opening of isophorone oxide (**1a**) was first attempted in a solvent–$(PhSe)_2$–$CH_2(CO_2Me)_2$ system in a divided cell using a Nafion 324 divider. Dimethyl malonate was employed as the proton source.[11] In order to elucidate the optimum conditions, we investigated the effect of various solvent–electrolyte–electrode systems. The results shown in Table I reveal that the desired β-hydroxy ketone **2a** was preferentially obtained in alcoholic solvents (entries 1, 4, and 6). In such solvents, either sodium perchlorate ($NaClO_4$) or lithium perchlorate ($LiClO_4$) proved a good choice as electrolyte. In contrast, a considerable proportion of the starting material **1a** was recovered intact when 3.5 F/mol of electricity was passed through the solution and a carbon electrode was used. When a lead electrode was used, the reaction was subjected to unidentified decomposition.

The broad scope and efficiency of **2a**, regardless of the amount of added diphenyl diselenide, is illustrated in Figure 1. Apparently, the C–O bond cleavage proceeds in the presence of diphenyl diselenide as a mediator in a wide range of molar ratios (with respect to the substrate **1a**) under a constant applied voltage of 3 V [corresponds to −1.30 to −1.35 V vs AgCl/Ag(0)]. Although an increase in the molar ratio of diphenyl diselenide to **1a** tends to improve the current efficiencies, high turnovers of the recycled mediator have been attained even with reduced amounts of diphenyl diselenide. Similarly, bis(4-methoxyphenyl) and bis(4-chlorophenyl) diselenides were used as mediators for the conversion of **1a** to **2a** in 65 and 80% yields, respectively.

Scheme II



It is noteworthy that the use of diphenyl ditelluride provides better results for both yields and current efficiencies at each molar ratio of the catalyst to **1a**. In spite of this fact, we routinely employed diphenyl diselenide as the mediator (electron carrier), after due consideration of commercial availability.

For comparison, the direct electroreduction of isophorone oxide (**1a**) was examined in various solvent–electrolyte systems. The results in Table II indicate that both THF–H_2O (9:1) and dry DMF solvent systems are suitable for the direct electroreduction. The electrolysis of **1a** in a THF–H_2O(9:1 v/v)–Bu_4NBF_4(0.1 M)–$CH_2(CO_2Et)_2$–(Pt) system at a constant current density of 12 mA/cm^2 (applied voltage: 13–16 V) gave the desired **2a** in 65% yield (entry 2). Lack of diethyl malonate, however, resulted in the formation of isophorone (**4a**) and its pinacol dimer **5a**, as major products (entry 1) (Scheme II).

Kariv-Miller et al. proposed a THF–H_2O–Bu_4NBF_4(0.5 M)–(Hg) system for the Birch-type reduction of ketones and aromatic nuclei.[12] However, we have experienced some difficulties in obtaining 1,3-diol **3a** by the reduction of **2a** in a THF–H_2O–Bu_4NBF_4(0.1 M)–(C) system.

The direct electroreduction also proceeded in a DMF–Et_4NOTs(0.5 M)–$CH_2(CO_2Et)_2$–(Pt) system (entry 3) under a constant current density of 12 mA/cm^2 (applied voltage: ca. 9–11 V). The yield was significantly lower with phenol as the proton source in the same electrolysis system (entry 4). The use of lead as a cathode affords the overreduction product **3a** in 24% yield (entry 5). The typical experimental procedure in entry 2 was extended to other substrates, and their results along with those obtained by the selenium-mediated indirect method are shown in Table III.

The indirect procedure appears to be superior to the direct method in terms of both product selectivities and yields. The indirect reductions are typically complete after passage of approximately 4.5 F/mol of electricity; in contrast, the direct method requires 10 F/mol. It is interesting to note that the direct electroreduction of pulegone oxide (**1f**) underwent a four-electron reduction to give the cor-

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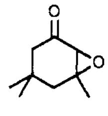
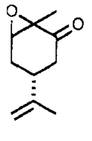
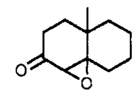
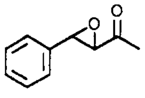
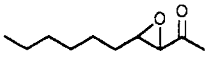
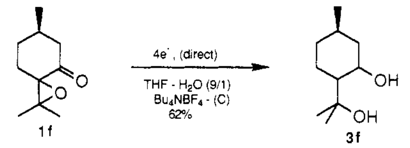
Table III. Comparison of Indirect and Direct Electroreductive Procedures with α,β-Epoxy Ketones 1

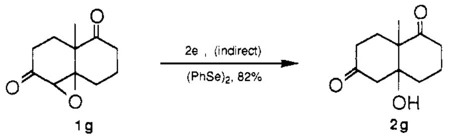
		β-hydroxy ketone 2, yield,[a] %	
entry	compd	direct[b]	indirect[c]
1	 **1a**	65	79
2	 **1b**	52	85
3	 **1c**	71	85
4	 **1d**	35[d]	70
5	 **1e**	41[e]	72

[a] Based on isolated products. [b] Direct electroreduction; substrate (1 mmol)-diethyl malonate (5 mmol) in a THF-H_2O(9:1 v/v)-Bu_4NBF_4(0.1 M)-(Pt)-(C) system under an applied voltage of 13-16 V (12 mA/cm^2) for 10.0 F/mol of electricity. [c] Indirect electroreduction; substrate (1 mmol)-$(PhSe)_2$ (0.02 mmol)-dimethyl malonate (5 mmol) in a MeOH-$NaClO_4$(0.2 M)-(Pt)-(Pt) system under an applied voltage of 3 V (30-5 mA/cm^2) for 4.5 F/mol of electricity. [d] Diol (30%) was obtained. [e] Diol (39%) was obtained.

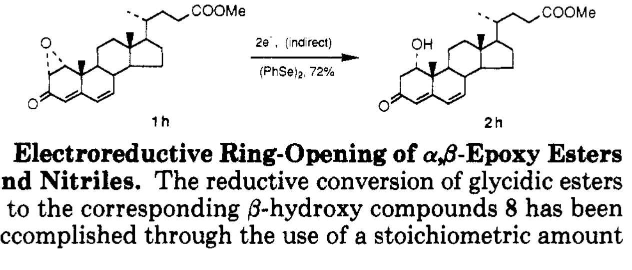
responding diol **3f** in 62% yield, while the indirect electroreduction of **1f** resulted in complete recovery of the starting material, presumably due to steric constraints of the substituents on the oxirane ring. The indirect electroreductive cleavage of the oxirane ring of polyfunctionalized compounds **1g** and **1h** proceeded specifically to give the corresponding β-hydroxy ketones **2g** and **2h** in 82 and 72% yields, respectively.



1f **3f**



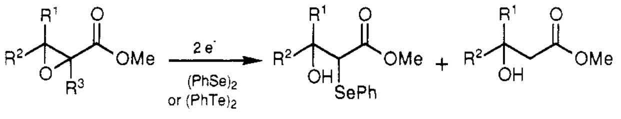
1g **2g**



1h **2h**

Electroreductive Ring-Opening of α,β-Epoxy Esters and Nitriles. The reductive conversion of glycidic esters **6** to the corresponding β-hydroxy compounds **8** has been accomplished through the use of a stoichiometric amount of sodium hydrogen telluride (NaTeH)[7a] and alkali metal.[13] Recently, samarium(II) iodide[14] and Na[PhSeB(OEt)$_3$][15] were proposed for this conversion. We have applied the above indirect electroreductive procedure to α,β-epoxy esters and nitriles.

The electroreduction of **6** in a MeOH-$NaClO_4$-(Pt) system was carried out in the presence of acetic acid as the proton source. Thus, the electrolysis of phenylglycidic ester **6a** with diphenyl diselenide [$(PhSe)_2$] (60 mol % based on **6a**) at room temperature resulted only in the formation of α-(phenylseleno)-β-hydroxy ester **7a** (entry 1, Table IV). However, increasing the temperature up to 50 °C led to the desired β-hydroxy ester **8a** in 75% yield, even with a catalytic amount of diphenyl diselenide (entry 2). The electrolysis of the α-phenylseleno ester **7a** at 50 °C afforded **8a** in 93% yield.

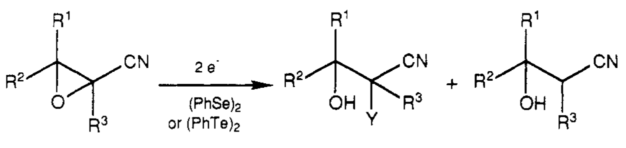


6 **7** **8**

a R^1=Ph, R^2=R^3=H
b R^1=R^2= -$(CH_2)_4$-, R^3=H
c R^1=Ph, R^2=CH_3, R^3=H
d R^1=R^2= -$(CH_2)_4$-, R^3=Me

The straightforward conversion of **6a** to **8a** could be accomplished at room temperature through the use of 2 mol % of diphenyl ditelluride [$(PhTe)_2$]. The comparative data are shown in Table IV. β,β-Dialkyl- and β-alkyl-β-aryl-α,β-epoxy esters **6b** and **6c** were smoothly converted to the corresponding β-hydroxy esters **8b** and **8c** (entries 4-6). However, α,β,β-trialkyl-α,β-epoxy ester **6d** could not be reduced to the β-hydroxy ester, and the starting epoxide **6d** was recovered unchanged.

The selenide or telluride anion assisted electroreduction of α,β-epoxy nitrile **9a** at room temperature (60 mol % diphenyl diselenide or diphenyl ditelluride) produced α-(phenylseleno)- or α-(phenyltelluro)-β-hydroxy nitriles **10a** (Y = SePh or TePh) (entries 1 and 3, Table V). In contrast, the electrolysis of **10a** at 50 °C with a catalytic amount of diphenyl diselenide (2 mol %) gave exclusively β-hydroxy nitrile **11a** (entry 13). The direct conversion of **9a** to **11a** could be achieved through electrolysis at 50 °C with a trace amount of diphenyl diselenide or ditelluride (2 mol %). These results reveal that the conversion of **9a** to **11a** apparently proceeds through α-(phenylseleno)- or α-(phenyltelluro)-β-hydroxy nitriles **10a** as the intermediate. As shown in entries 5-10 in Table V, the epoxy ring opening procedures of entries 2 and 4 were applied successfully to β-alkyl-β-aryl, β-aryl, and α,β-diaryl derivatives **9b-d**.



9 **10** Y = SePh TePh **11**

a R^1=R^2= -$(CH_2)_4$-, R^3=H
b R^1=Et, R^2=Ph, R^3=H
c R^1=Ph, R^2=R^3=H
d R^1=R^3=Ph, R^2=H

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Table IV. Indirect Electroreduction of α,β-Epoxy Esters 6 with (PhSe)$_2$ or (PhTe)$_2$[a]

entry	substrate	mediator[b] (mol %)	temp, °C	electricity,[c] F/mol	product, yield,[d] % 7	8
1	**6a**	A (60)	rt[e]	8.0	68	
2	**6a**	A (2)	50	6.5		75
3	**6a**	B (2)	rt	5.2		81
4	**6b**	A (2)	50	6.5		78
5	**6b**	B (2)	rt	6.0		80
6	**6c**	A (2)	50	6.0		78
7	**6c**	B (2)	rt	5.5		78
8	**6d**	A (2)	50	15.0	(recovd **6d**, 91)	
9	**6d**	B (2)	rt	15.0	(recovd **6d**, 90)	

[a] Carried out under Ar by using **6** (1 mmol) in an MeOH-NaClO$_4$(0.2 M)-(Pt)-(Pt) system in a divided cell. [b] A: (PhSe)$_2$. B: (PhTe)$_2$. Mole percent of the mediator to the substrates **6**. [c] Faradays/mole based on **6**. [d] Based on isolated products. [e] Room temperature.

Table V. Indirect Electroreduction of α,β-Epoxy Nitriles 9 with (PhSe)$_2$ or (PhTe)$_2$[a]

entry	substrate	mediator[b] (mol %)	temp, °C	electricity,[c] F/mol	product, yield,[d] % 10	11
1	**9a**	A (60)	rt[e]	8.0	69 (Y = SePh)	
2	**9a**	A (2)	50	6.1		82
3	**9a**	B (60)	rt	7.5	81 (Y = TePh)	
4	**9a**	B (2)	50	5.5		85
5	**9b**	B (2)	50	6.0		88
6	**9b**	B (2)	50	5.8		90
7	**9c**	A (2)	50	5.7		87
8	**9c**	B (2)	50	5.1		91
9	**9d**	A (2)	50	10.6		93
10	**9d**	B (2)	50	9.8		95
11	**10a** (Y = PhSe)	none	50	15.0	(recovd **10a**, 82)	
12	**10a** (Y = PhSe)	A (2)	rt	15.0	(recovd **10a**, 81)	
13	**10a** (Y = PhSe)	A (2)	50	3.2		92

[a] Carried out under Ar by using **9** (1 mmol) in a MeOH-NaClO$_4$(0.2 M)-(Pt)-(Pt) system in a divided cell. [b] A: (PhSe)$_2$. B: (PhTe)$_2$. Mole percent of the mediator to the substrates. [c] Faraday/mole based on the substrate. [d] Yield based on isolated products. [e] Room temperature.

The electroreductive ring-opening of epoxy ketones, esters, and nitriles is believed to proceed via an ionic mechanism involving an initial attack of electrogenerated phenyl selenide or telluride anions at the position α to the electron-withdrawing groups, as outlined by Yoshikoshi et al.[15] Subsequent nucleophilic attack of the second phenyl selenide or telluride anion on the α-phenylseleno or -telluro moiety of the adducts results in the formation of β-hydroxy carbonyls or nitriles, together with diphenyl diselenide or ditelluride, which may be recycled in the next reaction. This two-step selenation-deselenation (telluration-detelluration) sequence occurs smoothly at the position α to β-alkyl and β,β-dialkyl epoxy ketones, esters, and nitriles, regardless of the nature of the electron-withdrawing groups. However, when the α-alkyl substituent is a glycidic ester, nucleophilic attack by selenide or telluride anion is retarded, while no such steric effect due to α-substituents was observed in the α,β-epoxy nitrile, as shown in entries 9 and 10 of Table V.

In conclusion, electrogenerated phenyl selenide and telluride anions behave as highly chemo- and regioselective nucleophiles at the α position on α,β-epoxy ketones. Divalent selenide and telluride anions are stable enough to be recycled, and turnovers of these reagents reach about 40-70 in 1-20-mmol-scale operations, even when the potential is not controlled.[16] Especially noteworthy is the finding that selenium and tellurium reagents are recycled in their divalent states, a fact that permits the recovery of these reagents in the form of diphenyl diselenide or ditelluride.

Experimental Section

General Procedure. Melting points and boiling points as indicated by an air-bath temperature are uncorrected. GC analyses were carried out on a Yanagimoto Model G6800 instrument with a Quadrex bond-fused silica capillary column (methyl silicone: 0.25-mm film thickness, 25 m × 0.25 mm i.d.), integrated by using a SIC Chromatocorder-12 recorder. IR spectra were taken on a JASCO FT-IR-5000 spectrometer. NMR samples were prepared in CDCl$_3$ and recorded on a Varian VXR-500 spectrometer. Elemental analyses were performed in our laboratory on a Yanagimoto MT-3 instrument in combination with a Mettler UM-3 microanalytical balance.

Materials. (PhSe)$_2$ and (PhTe)$_2$ were prepared according to the method reported[17] and purified by recrystallization. Starting α,β-epoxy ketones were prepared from enones with alkaline hydrogen peroxide. α,β-Epoxy esters and α,β-epoxy nitriles were obtained by Darzen condensation.[18] Trisubstituted nitrile **9d** was prepared by the method reported.[19]

Apparatus. Unless otherwise noted, electrochemical reactions were carried out with a platinum plate (1.5 × 2 cm^2) as the anode and a platinum plate (3 cm^2) (for the indirect method) or a carbon plate (3 cm^2) (for direct electrolysis) as the cathode. A cylindrical beakerlike divided cell (3-cm diameter, 8-cm height, 50-mL volume) separated by a Nafion 324 film was used. During the electrolysis, argon gas was bubbled moderately through the catholyte from a fritted-glass ball.

Indirect Electroreduction of Isophorone Oxide (1a) with Diphenyl Diselenide. A General Procedure. A mixture of **1a** (154 mg, 1 mmol), dimethyl malonate (640 mg, 5 mmol), and diphenyl diselenide (6 mg, 0.02 mmol) was dissolved in a 0.2 M NaClO$_4$-MeOH solution (10 mL) and placed in the cathodic compartment of a divided cell. To the anodic compartment was added a 0.2 M NaClO$_4$-MeOH solution (10 mL). Prior to electrolysis, argon was bubbled through the electrolyte for 30 min and the entire mixture was electrolyzed at 15-20 °C under a constant applied voltage of 3 V [ca. −1.30 to −1.35 V vs AgCl/

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Ag(0)], during which an electric current decreased from 30 to 5 mA/cm^2. The electrolysis was continued until 4.5 F/mol of electricity was passed (8.5 h). Air was then bubbled for 10 min through the catholye, which was concentrated to half of its original volume and then poured into water. The mixture was taken up in ethyl acetate. The extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2; hexane–AcOEt, 5:1), to give 123 mg (79% yield) of **2a** along with $(PhSe)_2$ (5 mg, 83%). **2a**: mp 79–80 °C (from hexane) (lit.[7a] mp 79–79.5 °C); IR (KBr) 3400 (OH), 1705 (C=O); ^1H NMR (500 MHz) δ 1.04 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.60 (br s, 1 H, OH), 1.71–1.79 (m, 2 H, CH_2), 2.20 (br s, 2 H, CH_2), 2.34–2.44 (m, 2 H, CH_2); ^{13}C NMR (126 MHz) δ 28.4, 32.5, 33.1, 35.5, 50.0 (2 C), 54.0, 74.9, 210.8.

The electrolysis of 20 mmol of **1a** with $(PhSe)_2$ (0.02 mmol) was carried out with 15 mL of the same catholyte system as above, passing 10.5 F/mol of electricity, to give **2a** in 72% yield.

Direct Electrolysis in a THF–H$_2$O(9:1)–Bu$_4$NBF$_4$(0.1 M)–(C) System. Epoxy ketone **1a** (1 mmol) and diethyl malonate (5 mmol) dissolved in 0.1 M Bu_4NBF_4 in THF (9 mL)–H_2O (1 mL) were introduced into the cathodic compartment. The anodic compartment was filled with 0.1 M Bu_4NBF_4 in THF (9 mL)–H_2O (2 mL). The mixture was electrolyzed under a constant current density (12 mA/cm^2; applied voltage, 13–16 V) at room temperature until 10 F/mol of electricity was passed. The catholyte was poured into water (10 mL) and extracted with hexane–ether (1:1, 10 mL × 4). Combined organic layers were washed with brine (30 mL), dired (Na_2SO_4), and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2; hexane–AcOEt, 1:1), to give 102 mg (65%) of the β-hydroxy ketone **2a**.

Direct Electrolysis in a DMF–Et$_4$NOTs(0.5 M)–(C) System. Epoxy ketone **1a** (1 mmol) and diethyl malonate (5 mmol) dissolved in 0.5 M Et_4NOTs in DMF (10 mL) were introduced into the cathodic compartment. The anodic compartment was filled with 0.5 M Et_4NOTs in DMF (10 mL). The mixture was electrolyzed under a constant current density (12 mA/cm^2; applied voltage, 8–13 V) at room temperature until 7–8 F/mol of electricity was passed. The catholyte was poured into 1 N HCl (10 mL) and extracted with hexane–ether (1:1, 10 mL × 4). Combined organic layers were washed with brine (30 mL), dried (Na_2SO_4), and concentrated under vacuum, to give 98 mg (63%) of **2a** after purification by column chromatography.

Physical properties and spectral data of β-hydroxy ketones listed in Table III are as follows. **3-Hydroxy-2-methyl-(1-methylvinyl)cyclohexanone (2b)**[7g] (92:8 stereoisomers): bp 77 °C (0.21 mm); IR (neat) 3410 (OH), 1710 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 1.09 (d, J = 7 Hz, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.79–1.84 (m, 1 H, C=CCH), 2.12 (ddd, J = 3.5, 6, 14 Hz, 1 H, CH), 2.23–2.28 (m, 1 H, CH_2), 2.48 (ddd, J = 2.2, 3.5, 14 Hz, 1 H, CH), 2.53–2.56 (m, 1 H, CH_2), 2.83–2.89 (m, 1 H, CH_2), 3.56 (br s, 1 H, OH), 4.30 (m, 1 H, CHO), 4.74–4.77 (br s, 2 H, C=CH_2); ^{13}C NMR (126 MHz) (major isomer) δ 10.6, 20.5, 37.6, 39.9, 46.5, 49.2, 73.5, 109.9, 147.2, 211.1.

8a-Hydroxy-4a-methyl-2-decalone (2c): mp 118–119 °C (lit.[20] mp 120–121 °C); IR ($CHCl_3$) 3380 (OH), 1700 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 1.20 (s, 3 H, CH_3), 1.53–1.82 (m, 11 H, CH_2), 2.30–2.36 (m, 3 H, CH_2), 2.61 (br s, 1 H, OH); ^{13}C NMR (126 MHz) δ 20.4, 20.5, 20.7, 34.2, 34.3, 35.1, 36.5, 38.0, 51.7, 76.4, 211.3.

4-Hydroxy-4-phenyl-2-butanone (2d): bp 112–115 °C (0.3 mm) [lit.[21] bp 100 °C (0.45 mm)]; IR ($CHCl_3$) 3390 (OH), 1690 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 2.19 (s, 3 H, $COCH_3$), 2.81 (dd, J = 3.2, 17 Hz, 1 H, $COCH_2$), 2.89 (dd, J = 9.0, 17 Hz, 1 H, $COCH_2$), 3.35 (br s, 1 H, OH), 5.15 (m, 1 H, CHO), 7.26–7.40 (m, 5 H, Ph H); ^{13}C NMR (126 MHz) δ 30.7, 51.9, 69.8, 125.6, 127.6, 128.5, 142.7, 209.1.

4-Hydroxy-2-decanone (2e): bp 67 °C (0.48 mm) [lit.[21] bp 85 °C (0.3 mm)]; IR (neat) 3390 (OH), 1705 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 0.84 (t, J = 7 Hz, 3 H, CH_3), 1.20–1.50 (m, 10 H, CH_2), 2.14 (s, 3 H, $COCH_3$), 2.49 (dd, J = 9.2, 17.6 Hz, 1 H, $COCH_2$), 2.59 (dd, J = 2.8, 17.6 Hz, 1 H, $COCH_2$), 2.98 (br s, 1 H, OH), 3.99 (m, 1 H, OCH); ^{13}C NMR (126 MHz) δ 14.0, 22.6, 25.4, 29.2, 30.7, 31.7, 36.4, 49.9, 67.5, 210.0.

8a-Hydroxy-4a-methyldecalin-2,5-dione (2g): bp 87 °C (0.25 mm) (lit.[7b] mp 186–187 °C); IR (neat) 3380 (OH), 1720 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 1.42 (s, 3 H, CH_3), 1.54–1.58 (m, 1 H, CH_2), 1.77–1.81 (m, 1 H, CH_2), 1.89–1.94 (m, 1 H, CH_2), 2.10–2.26 (m, 2 H, CH_2), 2.28–2.34 (m, 1 H, CH_2), 2.36–2.49 (m, 4 H, CH_2), 2.64–2.71 (m, 1 H, CH_2), 2.75 (d, J = 15.5 Hz, 1 H, CH_2); ^{13}C NMR (126 MHz) δ 20.4, 27.9, 33.1, 36.3, 37.4, 50.6, 51.0, 77.4, 80.4, 210.5, 213.4.

Compound 2h: mp 120 °C; IR (KBr) 3736 (OH), 1736 (C=O), 1700 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 0.72 (s, 3 H, CH_3), 0.90 (d, J = 7 Hz, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.10–1.16 (m, 1 H, CH_2), 1.21–1.35 (m, 4 H, CH_2), 1.38–1.46 (m, 2 H, CH_2), 1.58–1.62 (m, 1 H, CH_2), 1.71–1.81 (m, 3 H, CH_2), 1.87–1.94 (m, 1 H, CH_2), 1.98–2.20 (m, 2 H, CH_2), 2.13–2.22 (m, 2 H, CH_2), 2.29–2.35 (m, 1 H, CH_2), 2.56 (dd, J = 2.6, 18 Hz, 1 H, $COCH_2$), 2.83 (dd, J = 3, 18 Hz, 1 H, $COCH_2$), 3.63 (s, 3 H, $COOCH_3$), 4.16 (br s, 1 H, CHO), 5.72 (br s, 1 H, HC=C), 6.13 (br s, 2 H, HC=C); ^{13}C NMR (126 MHz) δ 11.8, 17.7, 18.2, 20.1, 23.7, 27.9, 30.9, 31.0, 35.3, 37.6, 39.3, 40.9, 42.8, 43.5, 43.6, 51.5, 53.3, 55.6, 71.5, 122.9, 128.4, 141.8, 160.2, 174.6, 197.1. Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 75.11; H, 9.06.

1,3-Diols from epoxy ketones are as follows. **1-Phenylbutane-1,3-diol (3d)**: mp 95 °C (from hexane); IR ($CHCl_3$) 3370 (OH) cm^{-1}; ^1H NMR (500 MHz) δ 1.12 (d, J = 6.5 Hz, 3 H, CH_3), 1.66 (dt, J = 2.4, 14.6 Hz, 1 H, CH_2), 1.76 (dt, J = 10.0, 14.6 Hz, 1 H, CH_2), 3.06 (br s, 1 H, OH), 3.24 (br s, 1 H, OH), 4.04 (m, 1 H, CHO), 4.83 (dd, J = 2.9, 10.0 Hz, 1 H, CHO), 7.17 (m, 2 H, Ph H), 7.25 (m, 3 H, Ph H); ^{13}C NMR (126 MHz) δ 24.1, 47.0, 68.8, 75.3, 125.6, 127.6, 128.5, 144.4.

Decane-2,4-diol (3e) (70:30 stereoisomers) (major isomer): bp 136 °C (0.33 mm); IR (neat) 3370 (OH) cm^{-1}; ^1H NMR (500 MHz) δ 0.85 (t, J = 7 Hz, 3 H, CH_3), 1.17 (d, J = 3.3 Hz, 3 H, $OCCH_3$), 1.20–1.31 (m, 7 H, CH_2), 1.33–1.48 (m, 4 H, CH_2), 1.55 (dt, J = 2.5, 14.5 Hz, 1 H, CH_2), 3.02 (br s, 1 H, OH), 3.32 (br s, 1 H, OH), 3.82 (m, 1 H, CHO), 4.02 (m, 1 H, CHO); ^{13}C NMR (126 MHz) δ 14.0, 22.6, 24.2, 25.3, 29.3, 31.8, 38.2, 44.6, 69.2, 73.2. Minor isomer: bp 136 °C (0.38 mm); IR (neat) 3280 (OH); ^1H NMR (500 MHz) δ 0.85 (t, J = 7 Hz, 3 H, CH_3), 1.21 (d, J = 6.5 Hz, 3 H, $OCCH_3$), 1.23–1.59 (m, 12 H, CH_2), 3.12 (br s, 1 H, OH), 3.44 (br s, 1 H, OH), 3.91 (m, 1 H, CHO), 4.14 (m, 1 H, CHO), ^{13}C NMR (126 MHz) δ 14.1, 22.6, 23.5, 25.7, 29.3, 31.8, 37.4, 43.9, 65.5, 69.4.

2-(1-Hydroxy-1-methylethyl)-5-methylcyclohexanone (3f) (89:11 stereoisomers): mp 81 °C (from hexane–AcOEt); IR (neat) 3300 (OH) cm^{-1}; ^1H NMR (500 MHz) δ 0.90 (d, J = 6.5 Hz, 3 H, CH_3), 0.93–1.09 (m, 2 H, CH_2), 1.21 (s, 3 H, CH_3), 1.32–1.54 (m, 2 H, CH_2), 1.61–1.71 (m, 2 H, CH_2), 1.90–1.96 (m, 1 H, CH_2), 3.55 (br s, 1 H, OH), 3.56 (br s, 1 H, OH), 3.69 (dt, J = 4.2, 11 Hz, 1 H, CHO); ^{13}C NMR (126 MHz) (major isomer) δ 22.0, 23.7, 27.1, 29.9, 31.2, 34.5, 44.6, 53.4, 72.9, 75.0. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.74; H, 11.72.

Electroreduction of α,β-Epoxy Ester with Diphenyl Diselenide at Room Temperature. A Typical Procedure. A mixture of **6a** (178 mg, 1 mmol), AcOH (300 mg, 5 mmol), and $(PhSe)_2$ (187 mg, 0.6 mmol) was dissolved in a 0.2 M $NaClO_4$–MeOH solution (10 mL) and placed in the cathodic compartment. To the anodic compartment was added a 0.2 M $NaClO_4$–MeOH solution (10 mL). Ar was bubbled through the catholyte for 30 min, and the entire mixture was electrolyzed at 15–20 °C under a constant applied voltage of 3 V. During the electrolysis, an electric current decreased from 20 to 4 mA/cm^2. The electrolysis was continued until 8.0 F/mol of electricity was passed (17 h). The catholyte was worked up in the manner described above, and the crude products were purified by column chromatography (SiO_2; hexane–AcOEt, 5:1), to give 228 mg (68% yield) of **7a** and 75 mg of $(PhSe)_2$. **7a**: bp 132 °C (0.14 mm); IR (neat) 3440 (OH), 1750 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 3.12 (d, J = 4 Hz, 1 H, CH), 3.63 (s, 3 H, $COOCH_3$), 4.63 (d, J = 4 Hz, 1 H, CH and br s, 1 H, OH), 7.24–7.54 (m, 10 H, Ph H); ^{13}C NMR (126 MHz) δ 51.2, 52.5, 73.1, 127.9, 128.1, 128.3, 128.8, 128.9, 129.1, 134.9, 137.4, 172.3.

Indirect Electroreduction of α,β-Esters at 50 °C. A Typical Procedure. A mixture of **6a** (178 mg, 1 mmol), AcOH (300 mg, 5 mmol), and $(PhSe)_2$ (6 mg, 0.02 mmol) was dissolved in a 0.2 M $NaClO_4$–MeOH solution (10 mL) and placed in the cathodic compartment. To the anodic compartment was added 0.2 M $NaClO_4$–MeOH solution (10 mL). The mixture was elec-

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trolyzed in the manner described above at 50 °C under a constant applied voltage of 3 V (current, 20–4 mA/cm^2; electricity, 6.5 F/mol). The catholyte was worked up in the usual manner, to give 228 mg (68% yield) of **8a** and 5 mg (83%) of $(PhSe)_2$. **8a**: bp 126 °C (0.28 mm) [lit.[22] bp 140–143 (12 mm)]; IR (neat) 3426 (OH), 1734 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 2.60 (dd, J = 3.75, 16.3 Hz, 1 H, CH_2), 2.66 (dd, J = 9.23, 16.3 Hz, 1 H, CH_2), 3.22 (br s, 1 H, OH), 3.61 (s, 3 H, $COOCH_3$), 5.02 (dd, J = 3.75, 9.23 Hz, 1 H, CHO), 7.16–7.20 (m, 2 H, Ph H), 7.21–7.28 (m, 3 H, Ph H); ^{13}C NMR (126 MHz) δ 51.2, 52.5, 73.2, 128.3, 128.9, 129.1, 134.9, 172.3.

Spectral data of the products in Table IV are as follows. **Compound 8b**: bp 111 °C (0.36 mm); IR (neat) 3475 (OH), 1725 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.23–1.29 (m, 1 H, CH_2), 1.37–1.47 (m, 4 H, CH_2), 1.48–1.57 (m, 1 H, CH_2), 1.60–1.72 (m, 4 H, CH_2), 2.47 (s, 2 H, $COCH_2$), 3.33 (br s, 1 H, OH), 3.61 (s, 3 H, $COOCH_3$); ^{13}C NMR (126 MHz) δ 22.0, 25.6, 37.4, 45.1, 51.6, 69.9, 173.3.

Compound 8c:[23] bp 136 °C (0.22 mm); IR (neat) 3494 (OH), 1717 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.55 (s, 3 H, CH_3), 2.81 (d, J = 16 Hz, 1 H, CH_2), 2.99 (d, J = 16 Hz, 1 H, CH_2), 3.60 (s, 3 H, $COOCH_3$), 4.30 (br s, 1 H, OH), 7.22–7.26 (m, 1 H, Ph H), 7.32–7.35 (m, 2 H, Ph H), 7.45–7.46 (m, 2 H, Ph H); ^{13}C NMR (126 MHz) δ 30.6, 46.2, 51.7, 72.7, 124.4, 126.9, 128.3, 146.8, 173.1.

Electroreduction of 9 with Diphenyl Diselenide at Room Temperature. A Typical Procedure. A mixture of **9a** (127 mg, 1 mmol), AcOH (300 mg, 5 mmol), and $(PhSe)_2$ (187 mg, 0.6 mmol) dissolved in a 0.2 M $NaClO_4$–MeOH solution (10 mL) was degassed with Ar for 30 min and then electrolyzed at 15–20 °C under a constant applied voltage of 3 V in the cathodic compartment, the anolyte of which was a 0.2 M $NaClO_4$–MeOH solution (10 mL). During the electrolysis, an electric current decreased from 20 to 4 mA/cm^2. The electrolysis was continued until 8.0 F/mol of electricity was passed (21 h). The catholyte was worked up in the manner described above, to give 196 mg (69% yield) of **10a** (Y = SePh) and 62 mg of $(PhSe)_2$ after column chromatography (SiO_2; hexane–AcOEt, 5:1). **10a** (Y = SePh): bp 112 °C (0.25 mm); IR (neat) 3442 (OH), 2254 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.17–1.28 (m, 1 H, CH_2), 1.55–1.81 (m, 8 H, CH_2), 1.83–1.88 (m, 1 H, CH_2), 2.15 (br s, 1 H, OH), 3.69 (s, 1 H, CHCN), 7.33–7.41 (m, 3 H, Ph H), 7.71–7.73 (m, 2 H, Ph H); ^{13}C NMR (126 MHz) δ 21.6, 25.0, 35.3, 42.9, 72.6, 118.7, 127.3, 129.4, 129.6, 135.7.

Similar electrolysis of **9a** (0.2 mmol) with $(PhTe)_2$ (0.12 mmol) produced the adducts **10a** (Y = TePh): bp 131 °C (0.34 mm); IR (neat) 3445 (OH), 2250 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.15–1.28 (m, 1 H, CH_2), 1.50–1.89 (m, 8 H, CH_2), 1.90–1.95 (m, 1 H, CH_2), 2.18 (br s, 1 H, OH), 3.68 (s, 1 H, CHCN), 7.33–7.45 (m, 3 H, Ph H), 7.70–7.79 (m, 2 H, Ph H); ^{13}C NMR (126 MHz) δ 21.5, 25.0, 35.2, 42.9, 72.5, 118.6, 127.3, 129.3, 129.6, 135.7.

Indirect Electroreduction of α,β-Epoxy Nitriles at 50 °C. A Typical Procedure. A mixture of **9a** (127 mg, 1 mmol), AcOH (300 mg, 5 mmol), and $(PhSe)_2$ (6 mg, 0.02 mmol) dissolved in a 0.2 M $NaClO_4$–MeOH solution (10 mL) was electrolyzed in the manner described above at 50 °C under a constant applied voltage of 3 V (current, 20–4 mA/cm^2; electricity, 6.1 F/mol). The catholyte was worked up in the usual manner, to give 106 mg (82% yield) of **11a** and 5 mg (83%) of $(PhSe)_2$. **11a**: bp 91 °C (0.21 mm); IR (neat) 3426 (OH), 2238 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.25 (m, 1 H, CH_2), 1.49–1.71 (m, 9 H, CH_2), 2.12 (br s, 1 H, OH), 2.50 (s, 2 H, CH_2CN); ^{13}C NMR (126 MHz) δ 21.8, 25.0, 31.9, 36.8, 67.0, 117.5.

Spectral data of the compounds in Table VI are as follows. **Compound 11b**: mp 92 °C; IR (KBr) 3440 (OH), 2262 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.81 (t, J = 7.5 Hz, 3 H, CH_3), 2.04 (q, J = 7.5 Hz, 2 H, CH_2), 2.3 (br s, 1 H, OH), 2.04 (s, 2 H, CH_2CN), 7.29–7.32 (m, 2 H, Ph H), 7.37–7.43 (m, 3 H, Ph H); ^{13}C NMR (126 MHz) δ 7.7, 32.4, 34.1, 75.1, 117.3, 124.9, 127.8, 128.6, 142.7.

Compound 11c: mp 110 °C [lit.[24] bp 154–155 (1 mm)]; IR (neat) 3376 (OH), 2270 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 2.81 (br s, 1 H, OH), 3.12 (d, J = 6.5 Hz, 2 H, CH_2CN), 4.65 (dd, J = 6.5, 12.8 Hz, 1 H, CHO), 7.28–7.39 (m, 5 H, Ph H); ^{13}C NMR (126 MHz) δ 41.3, 62.1, 119.3, 127.8, 128.9, 129.7, 133.7.

Compound 11d (80:20 stereoisomers): mp 130 °C (lit.[25] mp 139.5–140.5 °C); IR (neat) 3442 (OH), 2252 (C≡N) cm^{-1}; ^{1}H NMR (500 MHz) δ 2.47, 2.61 (br s, 1 H, OH), 4.05, 4.14 (d, J = 5.5 and 11 Hz, 1 H, CHCN), 4.97, 4.98 (m, 1 H, CHO), 7.20–7.23 (m, 2 H, Ph H), 7.24–7.29 (m, 2 H, Ph H), 7.30–7.40 (m, 6 H, Ph H); ^{13}C NMR (126 MHz) (major isomer) δ 47.3, 76.1, 118.7, 126.2, 128.4, 128.5, 128.6, 128.8, 128.9, 132.4, 139.3.

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Supplementary Material Available: Current-potential curves for the electroreduction of **1a** in a MeOH–$NaClO_4$–(Pt) system with or without $(PhSe)_2$, in a THF/H_2O(9:1)–Bu_4NBF_4–(C) system, and in a DMF–Et_4NOTs–(C) system and ^{13}C NMR spectral data for compounds **3d–f**, **7a**, **8b**,**c**, **10a** (Y = SePh, TePh), and **11a**,**b** (14 pages). Ordering information is given on any current masthead page.

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