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Preparation of Cyclic α-Hydroxy Ketones from δ- and ε-Keto Acids Induced by the Generation of a Novel Acyl Anion Equivalent from the Carboxyl Group[1)]

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An improved method for the transformation of keto acids into cyclic α-hydroxy ketones, induced by the electrochemical generation of a novel acyl anion equivalent from the carboxyl group, has been developed. Both five- and six-membered rings were constructed by constant-current electrolysis of δ- and ε-keto acids in the presence of Bu_3P using an undivided cell equipped with a graphite anode and a Pt cathode. Attempts to prepare four- and seven-membered ring carbocycles were unsuccessful. The electrochemical reaction was found to be highly stereoselective when cyclization took place onto cyclopentanone and substituted cyclohexanone rings. Stereochemical aspects of the formation of bicyclic products, especially those having a bicyclo[4.3.0]skeleton, are discussed.

Key words acyl anion equivalent; electrochemical cyclization; α-hydroxy ketone; carboxylic acid; acyl tributylphosphonium ion; tributylphosphine

Although various acyl anion equivalents have been developed and are well recognized to be useful synthons for the direct introduction of a carbonyl moiety,[2)] C–C bond formation utilizing them is limited to intermolecular reactions since it is difficult to generate an acyl anion equivalent when an electrophilic site such as a carbonyl group exists in the same molecule. Thus, it is of interest for organic synthesis to develop a novel methodology to generate acyl anion equivalents applicable to the intramolecular reactions, although Shono *et al.* have reported that the preparation of cyclic α-hydroxy ketones, which would be formed when an acyl anion equivalent is allowed to react with an internal ketone, can be achieved alternatively by electroreductively promoted coupling of ketones with internal nitriles.[3,4)]

Recently, we have found that the partial reduction of carboxylic acids to the corresponding aldehydes can be achieved by constant-current electrolysis (CCE) of the acids in the presence of Ph_3P[5)] or Bu_3P[6)] in an undivided cell. Based on the proposed mechanism,[5b,6)] as well as the finding that an α-hydroxyalkyl phosphonium moiety is equivalent to an aldehyde, it was expected that the α-oxy ylide (B) generated by two-electron reduction of the acyl phosphonium ion (A) produced at the anode would function as a novel acyl anion equivalent (Chart 1). Our preliminary study confirmed that δ- or ε-keto acids can be transformed into cyclic α-hydroxy ketones by electrochemical reaction in the presence of Bu_3P when $R'=Bu$ in B.[7)] In this paper, we describe further studies conducted to establish the scope of this unique C–C bond formation reaction based on the addition of the acyl anion equivalent B generated from a carboxyl group onto an internal carbonyl group, and we propose a mechanism to explain the stereochemical outcome in the formation of the bicyclic products in these electrochemical reactions.

Results and Discussion

Recently, it was found that CCE of simple cyclic δ- and ε-keto acids (**1**) in the presence of Bu_3P generates an acyl anion equivalent such as **5** from the carboxyl group, leading to the formation of bicyclic α-hydroxy ketones (**2**) (Chart 2).[7)] In the previous work, the electrolysis conditions were scrutinized using 3-(2-oxocyclohexyl)propionic acid, **1a** ($n=2$, $m=1$) as a typical starting material. When the CCE was carried out in CH_2Cl_2 using an undivided

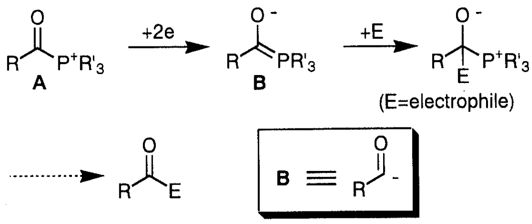
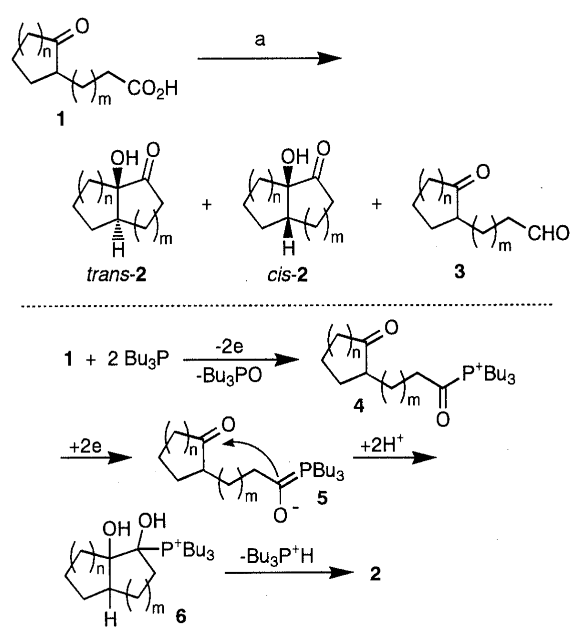


Chart 1



a) constant-current electrolysis, Bu_3P, CH_3SO_3H, $PhCH_2NEt_3Cl$, CH_2Cl_2, undivided cell, 0°C, graphite anode.

Chart 2

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cell equipped with two graphite plates as an anode and a cathode, the following four factors were found to be essential for the effective formation of **2a**: 1) addition of a proton source; 2) utilizing a chloride salt as a supporting electrolyte; 3) low reaction temperature; 4) applying a low electric current.

Thus, the electrochemical cyclization proceeded smoothly when a mixture of **1a**, Bu_3P, CH_3SO_3H, and $PhCH_2NEt_3Cl$ in CH_2Cl_2 was subjected to electrolysis with a constant current of 20 mA at 0 °C. However, the requirement (4) might be a problem from the synthetic point of view, because it takes a longer time to complete a reaction as CCE is performed at a lower electric current. In fact, the time taken to pass 4 F/mol of electricity even with only 3 mmol of **1a** was more than 16 h under the electrolysis conditions. Therefore, the effects of cathode materials on the electrochemical transformation of **1a** into **2a** were examined, in order to establish conditions enabling electrolysis at as high an electric current as possible, to give synthetically more satisfactory results. The results are summarized in Table 1.

As mentioned above, changing the value of the current from 20 to 60 mA with a graphite cathode resulted in a significant decrease in the yield of **2a**, along with some loss of stereoselectivity (runs 1 and 2). Using a Pt cathode at 60 mA gave the cyclized product in 68% yield, with an improved *trans*-selectivity (run 3). For the transformation of **1a** to **2a** by CCE at 60 mA, other cathode materials such as Sn, stainless steel, Pb, and Zn were almost as effective as Pt (runs 4—7). However, Pt was found to be the best cathode among them, and this was confirmed by the following results of CCE carried out at 20 and 100 mA (runs 8 and 9). Although applying the highest current (100 mA) caused a slight diminution in the yield of **2a**, the variation in the electrolysis current did not have as much influence on the cyclization as had been observed with a graphite cathode.

Table 1. Results of Constant-Current Electrolysis of Cyclic Keto Acids (**1a**—**h**) in the Presence of Bu_3P[a)]

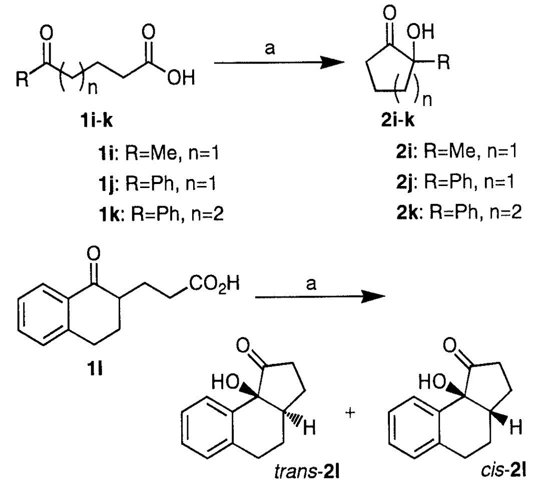
Run	Substrate			Current (mA)	Cathode material	Yield[b)] (%) of	
		n	*m*			**2** (*trans*:*cis*)[c)]	**3**
1	**1a**	2	1	20	Gr[d)]	64 (80:20)	—
2	**1a**	2	1	60	Gr[d)]	45 (76:24)	—
3	**1a**	2	1	60	Pt	68 (86:14)	—
4	**1a**	2	1	60	Sn	61 (85:15)	—
5	**1a**	2	1	60	SS[e)]	60 (86:14)	—
6	**1a**	2	1	60	Pb	57 (85:15)	—
7	**1a**	2	1	60	Zn	62 (82:18)	—
8	**1a**	2	1	20	Pt	64 (87:13)	—
9	**1a**	2	1	100	Pt	59 (87:13)	—
10	**1b**	1	1	60	Pt	29 (only *cis*)	44
11	**1c**	3	1	60	Pt	73 (72:28)	—
12	**1d**	4	1	60	Pt	63 (69:31)	—
13	**1e**	8	1	60	Pt	54 (83:17)	—
14	**1f**	2	0	60	Pt	—	—
15	**1g**	2	2	60	Pt	44 (59:41)	27
16	**1h**	2	3	60	Pt	—	73

a) A mixture of **1** (3 mmol), Bu_3P (9 mmol), CH_3SO_3H (6 mmol), and $PhCH_2NEt_3Cl$ (3 mmol) in CH_2Cl_2 was subjected to electrolysis in an undivided cell at 0 °C, until 4 F/mol of **1** was consumed. *b*) Isolated yield based on **1**. *c*) Determined by GLC of crude products. *d*) Graphite. *e*) Stainless steel.

The CCE of various cyclic keto acids (**1b**—**h**) was carried out under the conditions used in run 3. Cyclic δ-keto acids such as **1c**—**e** were transformed into bicyclic α-hydroxy ketones in good to fair yields (runs 11—13). In these reactions, *trans*-fused products predominated, similarly to the case of **1a**. It is noteworthy that the stereoselectivity in these systems is the opposite to that observed in Shono's reactions with 2-(2-cyanoethyl)cycloalkanones.[4)] The five-membered ring formation onto a cyclopentanone moiety did not gave a satisfactory result. Thus, the electrolysis of **1b** gave a bicyclic product **2b** in 29% yield along with a large amount of the corresponding aldehyde **3b**, although a reliably high *cis*-selectivity was observed (run 10). The electrolysis was also effective for the formation of a six-membered ring carbocycle from an ε-keto acid: **1g** was transformed into **2g** in a fair yield, although the stereoselectivity was lower than that for five-membered ring formation, and the corresponding aldehyde was afforded in a small amount (run 15). Under the same reaction conditions, **1f** and **1h** gave no cyclized products at all, indicating that the present reaction is not effective for the formation of four- and seven-membered rings (runs 14 and 16). Exclusive formation of the corresponding aldehyde was observed in the case of **1h**, while electrolysis of **1f** gave only highly polar compounds and no effort was made to isolate and identify them. It should be emphasized that, as in the case of **1a**, the electrolyses of **1b**, **1c**, **1e**, and **1g** under the improved conditions were completed within about 5.5 h, giving results comparable to or better than those reported previously with a graphite cathode at 20 mA (*cis*-**2b** 22%; **2c** 56%, 69:31; **2e** 53%, 84:16; **2g** 44%, 52:48).[7)]

The configurations of **2a**—**c**, **2e**, and **2g** were determined by comparison of their ^{13}C-NMR spectra with the reported data.[4)] The stereochemistry of each isomer of **2d** was assigned by employing the following ^{13}C-NMR correlation for bicyclo[*n*.*m*.0]alkan-1-ols: bridgehead alcohol carbons in *cis* isomers are consistently shifted downfield of the corresponding carbons in *trans* isomers.[8)] This has been proved to be the case in 1-hydroxy bicyclo[*n*.*m*.0]alkan-2-ones as well.[4)]

The present procedure was also applied to the transformation of acyclic keto acids **1i**—**k** into cyclic α-hydroxy ketones **2i**—**k** (Chart 3). The results are summarized in Table 2. The cyclization in the acyclic systems occurred in reasonable yields, and the formation of a five-membered ring proceeded more smoothly than that of a six-membered one, as can be seen in the cyclic systems (runs 1—3). It should be noted that Shono's method seems to fail in the preparation of **2j** and **2k** from γ- and δ-cyano aromatic ketones, respectively. In general, aromatic ketones are apt to undergo rapid two-electron reduction at a cathode, and this will not allow a species generated by initial one-electron reduction of a carbonyl group, that is, a ketyl radical, to cyclize on an unsaturated bond such as a cyano group, leading to C–C bond formation. In fact, the ketyl radical-based cyclization of 2-(2-cyanoethyl)-1-tetralone into **2l** was unsuccessful, resulting in the exclusive formation of the corresponding noncyclized cyano alcohol.[4)] Such a limitation of starting substrates was not encountered in the present cyclization, and the electrolysis



a) constant-current electrolysis, Bu_3P, CH_3SO_3H, $PhCH_2NEt_3Cl$, CH_2Cl_2, undivided cell, 0°C, graphite anode and Pt cathode.

Chart 3

Table 2. Results of Constant-Current Electrolysis of Various Keto Acids in the Presence of Bu_3P[a)]

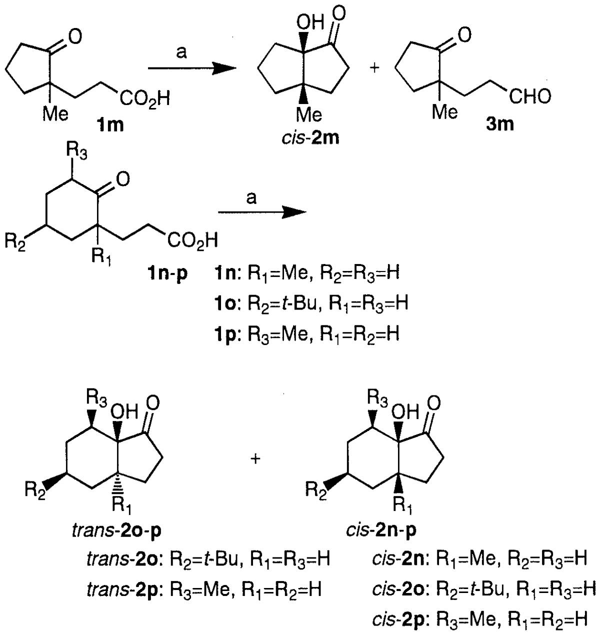
Run	Substrate	Products (yield %, *trans* : *cis*[b)])
1	**1i**	**2i** (37)
2	**1j**	**2j** (43)
3	**1k**	**2k** (22)
4	**1l**	**2l** (30, 67 : 33)
5	**1m**	*cis*-**2m** (50) **3m** (21)
6	**1n**	*cis*-**2n** (44)
7	**1o** (83 : 17)[c)]	**2o** (54, 91 : 9)
8	**1p** (79 : 21)[c)]	**2p** (58, 90 : 10)

a) See the footnote in Table 1. *b*) Determined by GLC of crude products. *c*) Diastereomeric ratio estimated from the ^{13}C-NMR spectrum.

was applied to the preparation of the tricyclic hydroxy ketone **2l** in a reasonable yield from **1l** (Table 2, run 4). The stereochemistry of **2l** was assigned from the chemical shift of the bridgehead alcohol carbon observed in the ^{13}C-NMR spectrum of each isomer, based on the correlation mentioned above.

We were also interested in the effects of substituents on the cycloalkanone ring upon the observed stereochemistry, as well as upon the yield in the formation of bicyclic products, especially those with a bicyclo[4.3.0] skeleton (Chart 4 and Table 2). As is apparent from the results of the electrolysis for **1m** and **1n** (runs 5 and 6), putting a methyl group at C-2 improved the yield of the product with a bicyclo[3.3.0] skeleton (*cf.* Table 1, run 10), and induced the exclusive formation of a *cis*-fused bicyclo[4.3.0] product (*cf.* Table 1, run 3). The configuration of *cis*-**2n** was determined by comparison of its ^{1}H- and ^{13}C-NMR spectra with the reported data.[4)] The stereochemistry of **2m** was assumed to be *cis*-fused, since the large strain expected in the *trans*-fused bicyclo[3.3.0] skeleton should make its formation almost impossible.

We next examined the electrochemical cyclization of 2-(2-carboxyethyl)cyclohexanones substituted at C-4 or C-6, such as **1o** and **1p**, each of which was a diastereomeric mixture. The reactions of these keto acids afforded the cyclized products as a mixture of only two isomers in satisfactory yields, although it was expected that the products would consist of four isomers, and a high *trans*-selectivity was retained in the formation of the bicyclo[4.3.0] skeleton (Table 2, runs 7 and 8).



a) constant-current electrolysis, Bu_3P, CH_3SO_3H, $PhCH_2NEt_3Cl$, CH_2Cl_2, undivided cell, 0°C, graphite anode and Pt cathode.

Chart 4

Based on the comprehensive spectral data for two known diastereomers with the *cis*-fused ring structure,[4)] not only the structure of *cis*-**2o** but also the mode of ring fusion in *trans*-**2o** was established. To determine the relative stereochemical arrangement in *trans*-**2o** as well as the configurations of *trans*- and *cis*-**2p**, difference nuclear Overhauser enhancement (NOE) experiments were conducted. However, the results were equivocal, because most of the proton signals for each of the products could not be definitely assigned due to poor peak separation even in the 500 MHz ^{1}H-NMR spectra. In addition, their transformation to the known bicyclo[4.3.0]nonan-1-ols[8)] failed, although it was reported that *trans*-isomers of **2c** and **2g** as well as *cis*-isomers of **2a**—**c**, **2g**, **2o**, and **2p** were converted to the corresponding bicyclo[4.3.0]nonan-1-ols by $LiAlH_4$ reduction followed by mesylation and reduction by $LiAlH_4$ or $LiEt_3BH$.[4)] Accordingly, the structure of *trans*-**2o** was tentatively determined on the basis that the major isomer of **1o** should have a thermodynamically stable *cis*-configuration, and its diastereomer ratio was not changed by merely stirring without passing any electric current under the reaction conditions; hence the configuration of *cis*-**1o** as a major isomer in the starting substrate should be reflected in that of the major bicyclic product. It seems reasonable that the major and the minor bicyclic products from **1p** are *trans*-**2p** and *cis*-**2p**, respectively, based on not only the argument that the major isomer of **1p** will have *cis*-configuration like that of **1o**, but also the following discussion on the origin of the stereochemical outcome observed in the present formation of bicyclo[4.3.0] systems.

The stereoselectivity in the cyclization of **1a**, **1l**, **1o**, and

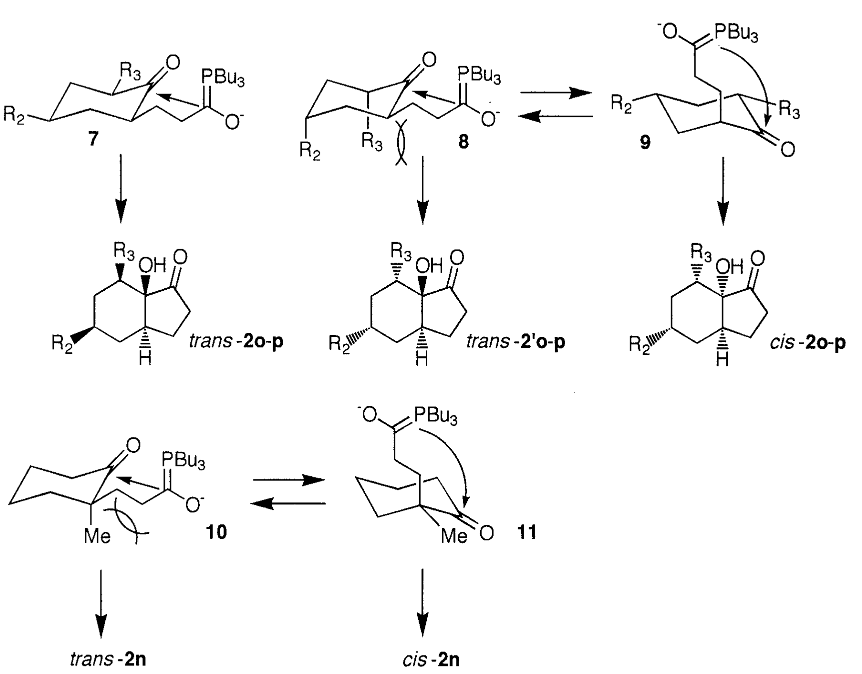


Chart 5

1p to bicyclo[4.3.0]nonanones can be explained by consideration of conformational effects. Since it is expected that the bulky ylide moiety as an acyl anion equivalent will highly prefer the equatorial direction of approach to the carbonyl carbon, the *trans*-fused products will be formed from the intermediates having the ylide moiety equatorial, such as **7** in Chart 5, while the nucleophilic site in the axial orientation like **9** will afford the *cis*-fused products. Thus, the *trans*-selectivity in the cyclization of **1a** and **1l** seems to reflect the extent of the nucleophilic intermediates existing in the conformation with the C-2 side chain in the equatorial orientation. The *trans*-selective cyclization of **1c**—**e** and **1g** can presumably be explained by a similar conformational factor.

In the cyclization of conformationally biased systems such as **1o** and **1p**, the configuration in the starting acids seems to affect the stereochemical outcome in the bicyclic products, in addition to the aforementioned conformational effects. The intermediates generated from *cis*-**1o** and *cis*-**1p** will adopt conformations having both substituents equatorial, like **7** in Chart 5 (R_2 = *tert*-Bu, R_3 = H or R_2 = H, R_3 = Me), giving *trans*-**2o** and *trans*-**2p**, respectively. In the case of *trans*-**1o** (R_2 = *tert*-Bu, R_3 = H), the side chain bearing the acyl anion equivalent will take the axial orientation due to the strong preference for the *tert*-butyl group to occupy the equatorial position, namely, the conformation **9** will be favored more than **8**, to afford *cis*-**2o**. Although the preferred conformation of the intermediate generated from *trans*-**1p** would be **8** with the bulkier side chain in the equatorial orientation, the equatorial direction of approach, giving *trans*-**2'p**, seemed to be sterically hindered by the 6-methyl substituent as depicted in Chart 5. Thus, it is most likely that the conformation **9** (R_2 = H, R_3 = Me) is of greater advantage for the cyclization, allowing us to conclude that *cis*-**2p** is the most reasonable structure for the cyclized product from *trans*-**1p**. This argument is supported by the exclusive formation of *cis*-**2n** in the electrolysis of **1n** having a 2-methyl substituent. Like the substituent at C-6 in *trans*-**1p**, the methyl group at C-2 prevents the equatorial direction of cyclization in the conformation **10** (Chart 5) with the nucleophilic side chain in the equatorial position, resulting in the exclusive formation of *cis*-**2n** *via* the conformation **11**.

Based on the results described so far, the present reactions are expected to provide a useful access to cyclic α-hydroxy ketones. They were found to proceed with high and predictable stereoselectivity when the cyclization takes place onto cyclopentanone and substituted cyclohexanone rings, constructing bicyclo[3.3.0] and bicyclo[4.3.0] skeletons. Although attempts to apply the acyl anion equivalent, generated electrochemically from acyl tributylphosphonium ions, to intermolecular C–C bond formation have so far been unsuccessful, further studies are in progress.

Experimental

Infrared (IR) spectra were taken on a JASCO VALOR-III spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained at 200 and 67.8 MHz on Varian VXR-200 and JEOL EX-270 spectrometers, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. For column chromatography, SiO_2 (Wakogel C-200) was used. Constant-current electrolysis (CCE) was carried out with a Hokuto Denko HA301, HA104, or HA105 potentiostat/galvanostat connected with a Hokuto Denko HF201 coulomb/amperehour meter.

Materials Cyclic keto acids **1a**—**e**, **1l**, and **1o** were prepared by transformation of the corresponding ketones into pyrrolidine enamines, followed by alkylation with methyl acrylate in dioxane[10] and hydrolysis in aqueous NaOH–DME. A similar procedure, except that the alkylation was carried out in MeOH,[11] afforded **1p**. Alkylation of 2-(ethoxycarbonyl)cyclohexanone with ethyl bromoacetate, ethyl 3-bromobutanoate, and ethyl 4-bromopentanoate, followed by hydrolysis and decarbonylation in AcOH–aqueous HCl[12] provided **1f**, **1g**, and **1h**, respectively. The keto acids **1i** and **1j** are commercially available and were used without further purification. The keto acid **1k** was prepared by alkylation of ethyl benzoylacetate with ethyl 4-bromopentanoate, followed by hydrolysis and decarbonylation in AcOH–aqueous HCl.[12] The cyclic keto acids **1m** and **1n** were obtained by alkylation of 2-methyl cyclohexanone and cyclopentanone, respectively, with methyl acrylate in the presence of a catalytic amount of *tert*-BuOK in *tert*-BuOH,[13] followed by hydrolysis in aqueous NaOH–DME.

General Procedure for the Electrolysis A CH_2Cl_2 solution (30 ml) of **1** (3 mmol), Bu_3P (9 mmol), CH_3SO_3H (6 mmol), and $PhCH_2NEt_3Cl$ (3 mmol) in an undivided cell equipped with a graphite plate anode (12.5 cm^2) and a Pt foil cathode (4.0 cm^2) was deoxygenated by bubbling N_2 for 20 min, and then subjected to CCE (60 mA) at 0 °C under an N_2 atmosphere. After 4.0 F/mol (*vs.* **1**) had been passed, the electrolyte was washed with 10% aqueous K_2CO_3 solution, and the aqueous layer was extracted with CH_2Cl_2 (50 ml × 2). The combined organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure, and the residue was subjected to silica gel column chromatography (*n*-hexane–ethyl acetate or CH_2Cl_2–acetone) to give the products. The products, *cis*-**2a**,[4] *cis*-**2b**,[4] **2c**,[4] **2e**,[4] **2g**,[4] **2i**,[9] *cis*-**2n**,[4] and *cis*-**2o**,[4] were identified by comparison of their spectroscopic data with those described in the cited references. Other products gave satisfactory physical data as shown below.

(1*RS*,6*RS*)-1-Hydroxybicyclo[4.3.0]nonan-9-one (*trans*-**2a**): IR (KBr): 3449, 1740 cm^{-1}. ^{1}H-NMR δ: 2.58—2.44 (2H, m), 2.13—1.99 (1H, m), 1.92—1.41 (8H, m), 1.30—1.16 (2H, m). ^{13}C-NMR δ: 217.45 (s), 75.10 (s), 46.09 (d), 35.26 (t), 30.50 (t), 25.97 (t), 25.09 (t), 24.37 (t), 20.88 (t). HR-MS *m/z*: Calcd for $C_9H_{14}O_2$: 154.0994. Found: 154.1000.

3-(2-Oxocyclopentyl)propanal (**3b**): IR (KBr): 1733 cm^{-1}. ^{1}H-NMR δ: 9.78 (1H, t, J=1.5 Hz), 2.63—2.55 (2H, m), 2.35—1.47 (9H, m). ^{13}C-NMR δ: 220.34 (s), 201.97 (d), 48.05 (d), 41.60 (t), 37.97 (t), 29.63 (t), 21.98 (t), 20.58 (t). HR-MS *m/z*: Calcd for $C_8H_{12}O_2$: 140.0838. Found: 140.0836.

(1*RS*,8*RS*)-1-Hydroxybicyclo[6.3.0]undecan-11-one (*trans*-**2d**): IR (KBr): 3463, 1740 cm^{-1}. ^{1}H-NMR δ: 2.47 (1H, dd, J=18.8, 7.9 Hz), 2.21—1.46 (17H, m). ^{13}C-NMR δ: 219.24 (s), 77.11 (s), 43.47 (d), 35.81 (t), 33.94 (t), 29.54 (2C, t), 27.64 (t), 27.04 (t), 26.15 (t), 21.33 (t). HR-MS *m/z*: Calcd for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1305.

(1*RS*,8*SR*)-1-Hydroxybicyclo[6.3.0]undecan-11-one (*cis*-**2d**): IR (KBr): 3447, 1741 cm^{-1}. ^{1}H-NMR δ: 2.34—2.09 (4H, m), 1.83—1.39 (13H, m). ^{13}C-NMR δ: 221.60 (s), 79.98 (s), 46.00 (d), 33.53 (t), 29.62 (t), 28.43 (t), 27.41 (2C, t), 24.96 (t), 24.76 (t), 22.64 (t). HR-MS *m/z*: Calcd for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1314.

4-(2-Oxocyclohexyl)butanal (**3g**): IR (KBr): 1709 cm^{-1}. ^{1}H-NMR δ: 9.77 (1H, t, J=1.7 Hz), 2.50—1.15 (15H, m). ^{13}C-NMR δ: 21.74 (s), 202.46 (d), 50.42 (d), 43.94 (t), 42.01 (t), 33.98 (t), 28.97 (t), 28.03 (t), 24.94 (t), 19.78 (t). HR-MS *m/z*: Calcd for $C_{10}H_{16}O_2$: 168.1151. Found: 168.1149.

5-(2-Oxocyclohexyl)pentanal (**3h**): IR (KBr): 1722, 1709 cm^{-1}. ^{1}H-NMR δ: 9.76 (1H, t), 2.49—1.19 (m, 17H). ^{13}C-NMR δ: 212.61 (s), 202.19 (d), 50.06 (d), 43.33 (t), 41.64 (t), 33.61 (t), 28.79 (t), 27.66 (t), 26.35 (t), 24.55 (t), 21.80 (t). HR-MS *m/z*: Calcd for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1312.

2-Hydroxy-2-phenylcyclopentanone (**2j**): IR (KBr): 3435, 1744 cm^{-1}. ^{1}H-NMR δ: 7.37—7.32 (5H, m), 3.00 (1H, s), 2.55—2.43 (3H, m), 2.39—2.17 (1H, m), 2.14—1.95 (1H, m), 1.89—1.72 (1H, m). ^{13}C-NMR δ: 218.53 (s), 140.65 (s), 128.39 (2C, d), 127.87 (d), 125.66 (2C, d), 80.40 (s), 37.53 (t), 35.65 (t), 17.11 (t). HR-MS *m/z*: Calcd for $C_{11}H_{12}O_2$: 176.0838. Found: 176.0837.

2-Hydroxy-2-phenylcyclohexanone (**2k**): IR (KBr): 3471, 1713 cm^{-1}. ^{1}H-NMR δ: 7.40—7.20 (5H, m), 3.00—2.89 (1H, m), 2.56—2.27 (2H, m), 2.06—1.60 (5H, m). ^{13}C-NMR δ: 212.16 (s), 139.69 (s), 128.66 (2C, d), 127.82 (d), 126.02 (2C, d), 79.66 (s), 38.53 (t), 38.47 (t), 27.87 (t), 22.61 (t). HR-MS *m/z*: Calcd for $C_{12}H_{14}O_2$: 190.0994. Found: 190.1005.

(3a*RS*,9b*SR*)-2,3,3a,4,5,9b-Hexahydro-9b-hydroxy-1*H*-benz[*e*]inden-1-one (*trans*-**2l**): IR (KBr): 3482 (s), 1734 cm^{-1}. ^{1}H-NMR δ: 8.15—8.12 (1H, m), 7.30—7.17 (3H, m), 3.07—2.85 (2H, m), 2.74—2.63 (1H, m), 2.33—1.87 (7H, m). ^{13}C-NMR δ: 213.26 (s), 138.54 (s), 136.03 (s), 129.43 (d), 128.54 (d), 126.33 (d), 125.89 (d), 71.84 (s), 44.53 (d), 36.34 (t), 29.62 (t), 23.09 (t), 20.90 (t). HR-MS *m/z*: Calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0993.

(3a*SR*,9b*SR*)-2,3,3a,4,5,9b-Hexahydro-9b-hydroxy-1*H*-benz[*e*]inden-1-one (*cis*-**2l**): IR (KBr): 3449 (br), 1743 cm^{-1}. ^{1}H-NMR δ: 7.43—7.40 (1H, m), 7.26—7.11 (3H, m), 3.11 (1H, s), 2.95—2.83 (2H, m), 2.55—2.45 (1H, m), 2.38—2.32 (2H, m), 2.22—2.10 (1H, m), 2.02—1.66 (3H, m). ^{13}C-NMR δ: 217.55 (s), 136.77 (s), 132.22 (s). 129.33 (d), 128.23 (d), 127.94 (d), 126.51 (d), 77.18 (s), 41.26 (d), 33.39 (t), 24.55 (t), 20.69 (t), 19.27 (t). HR-MS *m/z*: Calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0990.

(1*RS*,5*SR*)-1-Hydroxy-5-methylbicyclo[3.3.0]octan-2-one (*cis*-**2m**): IR (KBr): 3463 (br), 1740 cm^{-1}. ^{1}H-NMR δ: 2.56—2.44 (1H, m), 2.35—2.17 (1H, m), 2.09—1.66 (8H, m), 1.02 (3H, s). ^{13}C-NMR δ: 220.18 (s), 89.02 (s), 50.93 (d), 38.58 (t), 37.38 (t), 32.56 (t), 30.24 (t), 22.30 (t), 19.42 (q). HR-MS *m/z*: Calcd for $C_9H_{14}O_2$: 154.0994. Found: 154.0985.

3-(1-Methyl-2-oxocyclopentyl)propanal (**3m**): IR (KBr): 1733 cm^{-1}. ^{1}H-NMR δ: 9.77 (1H, t, J=1.65 Hz), 2.60—2.15 (4H, m), 1.98—1.64 (6H, m), 1.02 (3H, s). ^{13}C-NMR δ: 222.32 (s), 201.54 (d), 47.06 (s), 38.87 (t), 37.27 (t), 35.92 (t), 28.21 (t), 21.26 (t), 18.30 (q). HR-MS *m/z*: Calcd for $C_9H_{14}O_2$: 154.0994. Found: 154.0995.

(1*RS*,4*SR*,6*SR*)-1-Hydroxy-4-*tert*-butylbicyclo[4.3.0]nonan-9-one (*trans*-**2o**): IR (KBr): 3490, 2947, 1734 cm^{-1}. ^{1}H-NMR δ: 2.57—2.46 (1H, m), 2.39 (1H, s), 2.10—2.02 (1H, m), 1.91—1.42 (8H, m), 1.32—1.20 (1H, m), 1.15—1.05 (1H, m), 0.90 (9H, s). ^{13}C-NMR δ: 217.03 (s), 74.66 (s), 48.09 (d), 46.25 (d), 35.47 (t), 32.51 (s), 30.12 (t), 27.80 (3C, q), 25.59 (t), 24.04 (t), 21.64 (t). HR-MS *m/z*: Calcd for $C_{13}H_{22}O_2$: 210.1621. Found: 210.1619.

(1*RS*,2*RS*,6*RS*)-1-Hydroxy-2-methylbicyclo[4.3.0]nonan-9-one (*trans*-**2p**): IR (KBr): cm^{-1}. ^{1}H-NMR δ: 2.52—2.41 (1H, m), 2.11—1.12 (11H, m), 1.11 (3H, d, J=6.6 Hz). ^{13}C-NMR δ: 216.94 (s), 75.81 (s), 46.70 (d), 35.76 (d), 35.29 (t), 30.64 (t), 25.73 (t), 24.71 (t), 23.59 (t), 14.36 (q). HR-MS *m/z*: Calcd for $C_{10}H_{16}O_2$: 168.1151. Found: 168.1155.

(1*RS*,2*RS*,6*SR*)-1-Hydroxy-2-methylbicyclo[4.3.0]nonan-9-one (*cis*-**2p**): IR (KBr): 3499, 1740 cm^{-1}. ^{1}H-NMR δ: 2.72 (1H, s), 2.55—2.43 (1H, m), 2.33—2.12 (2H, m), 2.04—1.32 (9H, m), 0.79 (3H, d, J=6.9 Hz). ^{13}C-NMR δ: 219.24 (s), 79.55 (s), 41.28 (d), 32.90 (t), 30.41 (d), 28.77 (t), 23.51 (t), 20.43 (t), 19.73 (t), 13.59 (q). HR-MS *m/z*: Calcd for $C_{10}H_{16}O_2$: 168.1151. Found: 168.1150.

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References and Notes

1) This paper is dedicated to Professor Hans J. Schäfer on the occasion of his 60th birthday.
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