with LDA (from 200 mg diisopropylamine in 2 mL of THF and 0.77 mmol of BuLi in hexane), followed by quenching with D_2O at −40 °C, **5-deuterio-5,7-diphenyldibenz[*c*,*e*]azepine** (**20**, R = C_6H_5) was obtained. (Only the ^1H NMR signal at 5.183 ppm disappeared).

5,7-Diphenyldibenz[*c*,*e*]azepin-5-ol (25). A solution of 120 mg (0.35 mmol) of **6** (R = R′ = C_6H_5) in 7 mL of chlorobenzene was stirred vigorously under ambient atmosphere at 60 °C with 10 mL of 50% aqueous NaOH containing 160 mg of tetrabutylammonium bromide. After 4 h the temperature was raised to 85 °C and stirring was continued for another 20 h. Phase separation and evaporation of the chlorobenzene under reduced pressure followed by flash chromatography on silica gel (with 20% ether in pentane as eluent) afforded 104 mg (83%) of **25** as colorless crystals; mp 136–137 °C (from ether–pentane); 300-MHz ^1H NMR (acetone-d_6) δ 6.889 (s, 5), 7.028–7.729 (m, 12), 8.338 (dd, $J_{3,2}$ = 1.8 Hz, $J_{3,4}$ = 7.1 Hz, H4); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 361 ($M^{\bullet+}$, 5), 360 [$(M - H)^+$, 16], 344 [$(M - OH)^+$, 2], 282 ($C_{20}H_{12}NO^+$, 3), 257 ($C_{19}H_{15}N^{\bullet+}$, 55), 256 ($C_{19}H_{14}N^+$, 100), 241 ($C_{19}H_{13}^+$, 4), 178 ($C_{13}H_8N^+$, 27).

When the procedure was repeated under exclusion of air, the entire starting material was recovered unchanged.

Crystals for X-ray analysis were obtained by slow recrystallization (during 10 days) from acetone. The crystal unit consisted of two independent pairs [**25(i)** and **25(ii)**] that differed only in the relative angle of the two phenyl groups. Data were measured on a PW110/20 Philips four-circle computer-controlled diffractometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 15 centered reflections in the range of 9° < θ < 12°. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 45°. The scan width, Δω, for each reflection was 1° with a scan time of 20 s. Background measurements were made for another 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN direct method analysis.[39] After several cycles of refinements[40] the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0.5 Å to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight, w, is $1/\sigma(F_o)^2$. A final different Fourier synthesis map showed several peaks less than 0.5 eÅ^{-3} scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and the other pertinent crystallographic data are as follows: formula, $C_{26}H_{19}NO$; molecular weight 361.4; space group $P2_1/n$; a = 16.850 Å; b = 20.565 Å; c = 11.565 Å; α = 90°; β = 101.44°; γ = 90°; V = 3928 Å^3, Z = 8; ρ_{calcd} = 1.22 g cm^{-3}; μ(Mo Kα) = 0.40 cm^{-1}; number of unique reflections 4922; reflections with $I \geq 3\sigma(I)$ = 2595; R = 0.086; R_w = 0.096. The positional and thermal parameters, selected angles, and bond lengths obtained are summarized in Tables 1–10 of the supplementary material of this paper and a stereoscopic view of **25(i)** is given in Figure 1.

1-Benzyl-1a,9b-dihydrophenanthro[9,10-*b*]azirine (26). To a cold solution (0 °C) of 2.0 g (7.3 mmol) of the bromide **8** (R = R′ = H, X = Br)[20] in 60 mL of anhydrous ether was added 2.0 g (19 mmol) of freshly distilled benzylamine in 20 mL of the same solvent. The mixture was heated to 25 °C and stirred at this temperature for 60 min. Washing with cold 5% aqueous $NaHCO_3$ and water followed by removal of the solvent and HPLC separation on an Altech R.P. 18 column (80% aqueous MeOH served as eluent) afforded 185 mg (9%) of **26** (R = H) of properties identical with those of an authentic sample.[1]

5-Methyl-6-benzyl-5*H*-dibenz[*c*,*e*]azepinium Bromide (27, R = CH_3, R′ = $CH_2C_6H_5$). A solution of 2.0 g (6.9 mmol) of bromide **8** (R = H, R′ = CH_3, X = Br) and 1.4 g (13.8 mmol) of benzylamine in 150 mL of anhydrous benzene was stirred under reflux for 20 h. The colorless precipitate (2.3 g, 88%) proved to be pure **27**, R = CH_3, R′ = $CH_2C_6H_5$: mp dec 210 °C; 200-MHz ^1H NMR ($CDCl_3$) δ 1.081 (d, 3, J = 7 Hz, CH_3), 5.323 (q, 1, J = 2 Hz, $CHCH_3$), 5.799 (s, 2, $CH_2C_6H_5$), 7.231–8.467 (m, 13, aromatic), 10.292 (s, 1, CH=N). Anal. Calcd for $C_{22}H_{20}BrN$: C, 69.85; H, 5.33; Br, 21.12; N, 3.70. Found: C, 70.05; H, 4.87; Br, 21.20; N, 3.62.

Acknowledgment. We wish to thank Dr. Shmuel Cohen for his help in X-ray analysis, Professor von Schleyer for most useful discussion, and the Fund for Basic Research, The Israel Academy of Sciences and Humanities for financial support of this study.

Supplementary Material Available: Tables of crystallographic data for compound **25** (9 pages). Ordering information is given on any current masthead page.

(39) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 78. *A System of Computor Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, Universities of York, England and Louvain, Belgium.

(40) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University, Jerusalem, using the SHELX 1977 structure determination package.

Electroorganic Chemistry. 99. β-Acetoxylation and β-Halogenation of *N*-Methoxycarbonyl Cyclic Amines[1]

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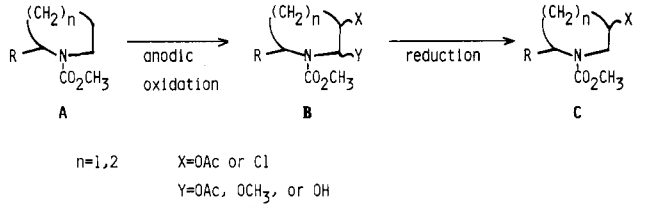
Received April 1, 1986

Anodic oxidation of *N*-(methoxycarbonyl)pyrrolidines (n = 1) and -piperidines (n = 2) (**A**) gave α,β-disubstituted compounds **B**, in which the α-substituent was an acetoxy, hydroxy, or methoxy group and the β-substituent was an acetoxy group or halogen atom. The α-substituents of **B** were easily removed by $NaBH_4$ under acidic conditions to give β-substituted compounds **C**. A reaction mechanism involving the formation of α,β-unsaturated intermediate **E** followed by anodic oxidation of **E** or attack of halogen-active species on **E** has been presented for the anodic α,β-disubstitution.

Functionalization of a less reactive methylene group is one of the most interesting current topics, while generally effective methods have not always been found yet. One of the methods hitherto exploited may be remote oxida-

0022-3263/87/1952-0536$01.50/0

Scheme I

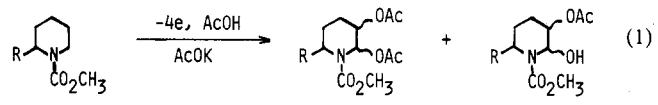


tion, in which a methylene group at a remote position from an activating group can be oxidized with some efficient selectivity.[2] We report herein a convenient method for introducing an acetoxy group or halogen atom to the β-methylene group of *N*-methoxycarbonyl cyclic amines **A**.

We have already studied anodic α-methoxylation[3] or α-hydroxylation[4] of a variety of carbamates. In continuing this study, we have found that the anodic oxidation of **A** under certain conditions gave α,β-disubstituted products **B** in satisfactory yields instead of α-monosubstituted ones. Since the α-substituent of **B** is easily removable by reduction to give β-substituted compounds **C**, the overall transformation from **A** to final products **C** corresponds to a β-functionalization of **A** (Scheme I). This report describes these results together with a discussion of the reaction mechanism of the α,β-disubstitution.

Results and Discussion

Anodic α,β-Diacetoxylation of *N*-(Methoxycarbonyl)piperidines. Although the anodic oxidation of *N*-(methoxycarbonyl)piperidines **1a–d** in methanol using $(C_2H_5)_4NOTs$ as a supporting electrolyte gives α-methoxylated products,[3] the anodic oxidation of **1a–d** in acetic acid containing AcOK as a supporting electrolyte gave α,β-diacetoxylated products **2** and/or α-hydroxy-β-acetoxy compounds **3** (eq 1). The compounds **2** are unstable under



(1)

a, R=H
b, R=CH_3
c, R=n-C_3H_7
d, R=CH_2COCH_3

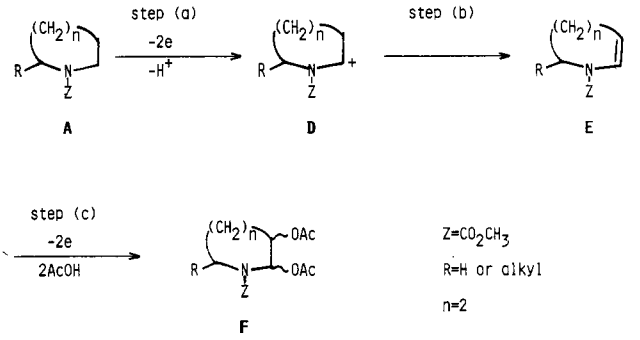
acidic conditions; workup of the acidic electrolyzed solution with water (method a) gave only **3**. Careful workup of the electrolyzed solution with cold aqueous $NaHCO_3$ (method b) was necessary to get **2**. Products were isolated as mixtures of stereoisomers.[5] The yields of **2** and **3** are summarized in Table I.

Table I. Anodic Oxidation of *N*-(Methoxycarbonyl)piperidines 1a–d

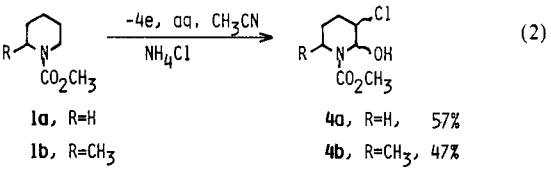
run	compd	method[a]	isolated yield, % 2	3
1	**1a**	a		**3a** (88)
2	**1a**	b	**2a** (61)	**3a** (20)
3	**1b**	a		**3b** (92)
4	**1b**	b	**2b** (34)	**3b** (45)
5	**1c**	a		**3c** (93)
6	**1d**	a		**3d** (53)

[a] See text.

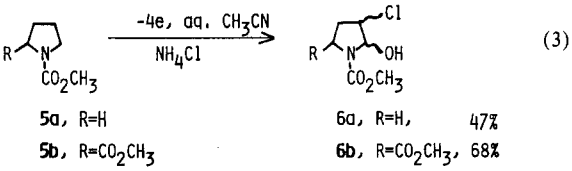
Scheme II



Anodic α-Hydroxy-β-chlorination of *N*-(Methoxycarbonyl)piperidines and -pyrrolidines. Anodic oxidation of *N*-(methoxycarbonyl)piperidines **1a,b** and -pyrrolidines **5a,b** in aqueous acetonitrile containing NH_4Cl gave α-hydroxy-β-chlorinated products **4a,b** and **6a,b**, respectively, in satisfactory yields (eq 2 and 3).[6] This type

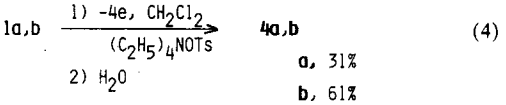


(2)

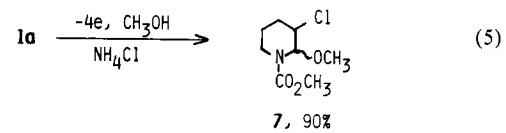


(3)

of β-chlorination was also achieved by anodic oxidation in dichloromethane containing $(C_2H_5)_4NOTs$ (eq 4) or in



(4)



(5)

methanol containing NH_4Cl (eq 5).[6] On the other hand, the anodic oxidation of **A** using NH_4Br or NH_4I as a supporting electrolyte did not give α-hydroxy-β-brominated or α-hydroxy-β-iodinated products but resulted in the recovery of **A**. Preparation of the latter compounds was achieved by the method as described below.

Reaction Mechanism of Anodic α,β-Diacetoxylation of *N*-(Methoxycarbonyl)piperidines. Acetoxylation of

(1) A part of this study was preliminarily reported: Shono, T.; Matsumura, Y.; Onomura, O.; Kanazawa, T.; Habuka, M. *Chem. Lett.* **1984**, 1101.

(2) For examples: (a) Heusler, K.; Wieland, P.; Meystre, Ch. *Org. Synth.* **1965**, *45*, 57. (b) Mihailović, M. Lj.; Čeković, Ž.; Stanković, J. *J. Chem. Soc., Chem. Commun.* **1969**, 981. (c) Becker, Y.; Byrd, L. R.; Miller, L. L. *J. Am. Chem. Soc.* **1974**, *96*, 4718. (d) Breslow, R.; Corcoran, R. J.; Snider, B. B.; Doll, R. J.; Khanna, P. L.; Kaleya, R. *Ibid.* **1977**, *99*, 905. (e) Haines, A. H. In *Methods for the Oxidation of Organic Compounds*; Katrizky, A. R., Meth-Cohn, O., Ress, C. W. Eds.; Academic: New York, 1985; p 49.

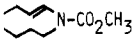
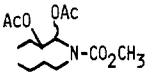
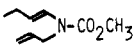
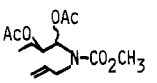
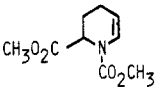
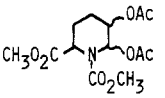
(3) Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264.

(4) Shono, T.; Matsumura, Y.; Kanazawa, T.; Habuka, M.; Uchida, K.; Toyoda, K. *J. Chem. Res. Synop.* **1984**, 320; *J. Chem. Res. Miniprint* **1984**, 2876.

(5) The fact that the products were α,β-disubstituted compounds is supported by satisfactory spectroscopic and/or elemental analyses. Furthermore, the result that the elimination of α-substituent from each of the products gave a single compound in high yields[1] also supports that each of the products was really a mixture of cis and trans isomers.

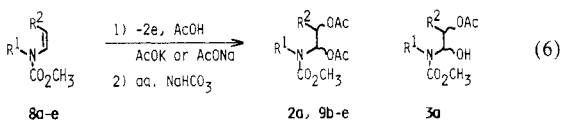
(6) Mixtures of stereoisomers were isolated.

Table II. Anodic Oxidation of α,β-Unsaturated Compounds 8a–e[a]

run	compd struct	compd no.	supp electrolyte	isolated yield, % struct	isolated yield, % no.
1		**8a**	AcOK		**2a** (65), **3a** (22)
2		**8b**	AcONa		**9b** (55)
3		**8c**	AcONa		**9c** (76)
4		**8d**	AcONa		**9d** (83)
5		**8e**	AcOK		**9e** (75)

[a] The workup was carried out by method b. See text.

the less reactive β-position of **A** may proceed through the following three steps: (a) formation of α-cation intermediate **D** by the anodic oxidation of **A**; (b) conversion of **D** to α,β-unsaturated compound **E**;[7] (c) subsequent anodic oxidation of **E** to diacetoxylation product **F**, as shown in Scheme II. The intermediary formation of **E** is reasonable since **8a** was observed in the course of the anodic oxidation of **1a**, and the anodic oxidation of independently prepared α,β-unsaturated compounds **8a–e**[8] in acetic acid also gave **2a**, **9b–e**, and **3a** (eq 6).[9] Yields of these products are shown in Table II.



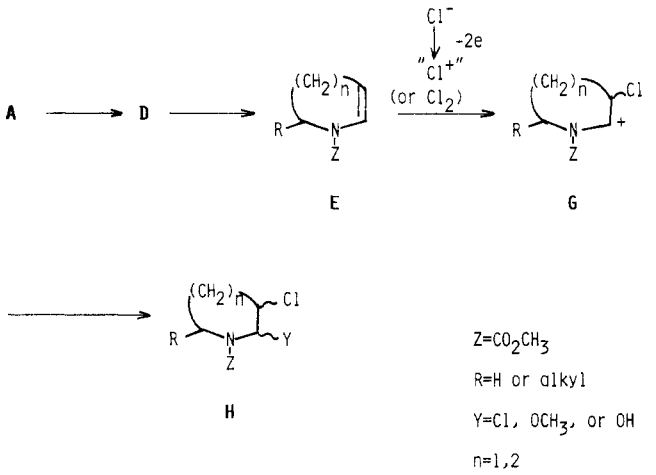
(6)

The transformation of **E** to **F** may proceed by oxidation of **E** to the cation radical, attack by a nucleophile, oxidation of the resulting radical to the cation, and finally attack again by a nucleophile.[10]

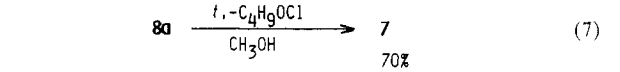
Reaction Mechanism of Anodic β-Chlorination of *N*-(Methoxycarbonyl)piperidines and -pyrrolidines. The anodic α-hydroxy- or α-methoxy-β-chlorination may also proceed by a mechanism similar to the anodic α,β-diacetoxylation except step (c) (Scheme III). Thus, the intermediate **E** may be generated in situ from **D**.[11]

The intervention of **E** was strongly suggested by the fact that **8a** was observed in the anodic oxidation of **1a**, that the anodic oxidation of independently prepared **8a** in a reaction system of aqueous CH_3CN–NH_4Cl and CH_2Cl_2–$(C_2H_5)_4NOTs$ gave the β-chlorinated product **4a** in 79% and 34% yield, respectively, and that **7** was formed by anodic oxidation of **8a** in methanol containing NH_4Cl with 82% yield.

Scheme III



The β-chlorination of **E** can be rationalized by the attack **E** by "Cl^+"[13] or Cl_2 generated by anodic oxidation of Cl^-,[14,16] followed by the conversion of the intermediate cation **G** to **H** since β-chlorination of α,β-unsaturated compound **E** (**8a**) was achieved by treating **E** with *tert*-butyl hypochlorite (eq 7).[6] It is well-known that "Cl^+" or Cl_2 generated anodically from Cl^- attacks alkenes.[15b,17]



(7)

This mechanism suggests that the anodic oxidation of **E** in the presence of Br^- or I^- makes β-bromination and β-iodination of **E** possible, since Br^- and I^- are more easily oxidizable than Cl^-.[18] Thus, the anodic oxidation of **8a,b,f** under the reaction conditions shown in eq 8 gave β-brominated and β-iodinated products **10–12**.[6]

(7) α-Acetoxylated compounds may intervene between **D** and **E**.

(8) (a) Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y. *Tetrahedron Lett.* **1982**, *23*, 1201. (b) Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y.; Yamane, S.; Kanazawa, T.; Aoki, T. *J. Am. Chem. Soc.* **1982**, *104*, 6697.

(9) Oxidation of enamines: Hickmott, P. W. *Tetrahedron* **1982**, *38*, 3363.

(10) Oxidation potentials of **8a** and **8b** were E_p = 1.37 and 1.59 V vs. SCE, respectively, in CH_3CN–0.1 N $LiClO_4$ (100 mV/s).

(11) The reaction conditions [CH_2Cl_2–$(C_2H_5)_4NOTs$, aqueous CH_3CN–NH_4Cl, CH_3OH–NH_4Cl] became acidic while the electrolysis proceeded.[12]

(12) The electrochemical generation of acids has been known. For example: Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1985**, *43*, 557.

(13) "Cl^+" denotes the positive halogen species generated from Cl^-.

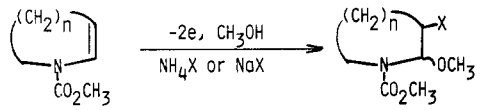
(14) Under the conditions of the CH_2Cl_2–$(C_2H_5)_4NOTs$ system, Cl^- may be generated by the cathodic reduction of CH_2Cl_2.[15a]

(15) (a) Siegermen, H. In *Technique of Electroorganic Synthesis*; Weinberg, N. L., Ed.; Wiley: Chichester, 1974; p 828. (b) Weinberg, N. L. In Reference 15a, p 373.

(16) The potentials at which oxidation begins to occur in CH_3CN–0.1 N $LiClO_4$: 1.05 V vs. SCE for **8a**; 1.08 V vs. SCE for **8b**; 0.94 V vs. SCE for Cl^- (100 mV/s).

(17) Electrophilic attack of halogens to enamines. See ref 9.

(18) Yoshida, K. In *Electrooxidation in Organic Chemistry*; Wiley: Chichester: 1984; p 88.



(8)

8b, n=1 — 10p, n=1, X=Br, 42% from 8b

8a, n=2 — 10q, n=1, X=I, 38% from 8b

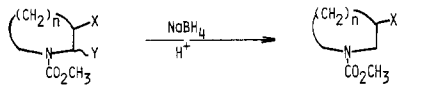
8f, n=3 — 11p, n=2, X=Br, 81% from 8a

11q, n=2, X=I, 81% from 8a

12p, n=3, X=Br, 70% from 8f

12q, n=3, X=I, 66% from 8f

Elimination of α-Substituents. α-Substituents (Y) of **B** were found to be reductively removable as exemplified by the reduction of **9b** and **4a** with $NaBH_4$ under acidic conditions (eq 9). Accordingly, the combination of this reductive elimination with the anodic α,β-difunctionalization makes the facile transformation of **A** to **C** possible.

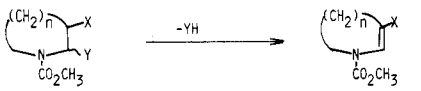


(9)

9b, n=1, X=Y=OAc — 13, n=1, X=OAc, 82% from 9b

4a, n=2, X=Cl, Y=OH — 14, n=2, X=Cl, 80% from 4a

α-Substituents of **B** were also eliminated by heating **B** under acidic conditions to afford β-substituted α,β-unsaturated compounds such as **15** and **16** (eq 10).



(10)

6a, n=1, X=Cl, Y=OH — 15, n=1, X=Cl, 94% from 6a

11p, n=2, X=Br, Y=OCH3 — 16, n=2, X=Br, 96% from 11p

Experimental Section

Infrared (IR) spectra were recorded on a Hitachi 215 or 260-10 spectrometer. Proton nuclear magnetic resonance spectra (^1H NMR) were measured on Varian Associates EM-360 or EM-390 spectrometer with chemical shifts given in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were obtained on JEOL IMS-DX 300 instrument. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Boiling and melting points are uncorrected.

Anodic Oxidation. Anodic oxidation was carried out with use of a dc power supply (GP 050-2) of Takasago Seisakusho, Ltd. A glass beaker (50 mL) equipped with Pt-plate anode (20 mm × 20 mm) and carbon-rod cathode (8-mm o.d.) was used as an electrolysis cell.

Materials. The preparation of **1a,b**,[3] **5a**,[3] **5b**,[8b] **8a–d**,[8b] and **8e**[19] has been reported. Compounds **1d**[20] and **8f**[8b] were prepared according to the reported method.

α-Acetonyl-*N*-(methoxycarbonyl)piperidine (1d) was prepared by the reaction of α-methoxy-*N*-(methoxycarbonyl)-piperidine[3] with isopropenyl acetate in the presence of $TiCl_4$ in 69% yield: IR (neat) 2950, 2920, 1700, 1452, 1270, 1175, 762 cm^{-1}; NMR (CCl_4) δ 1.46 (br s, 6 H), 2.16 (s, 3 H), 2.48 (d, J = Hz, 2 H), 2.85 (dt, J = 3 and 14 Hz, 1 H), 3.67 (s, 3 H), 3.96 (dd, J = 14 and 3 Hz, 1 H), 4.52–4.83 (m, 1 H). Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.42; H, 8.75; N, 6.74.

***N*-(Methoxycarbonyl)aza-2-cycloheptene (8f)**: 86% yield from the corresponding α-methoxylated compound;[21] bp 94–95 °C (25 mm); IR (neat) 2940, 2860, 1712, 1655, 1448, 1220, 788 cm^{-1}; NMR (CCl_4) δ 1.55–1.92 (m, 4 H), 2.09–3.34 (m, 2 H), 3.59–3.84 (m, 2 H), 3.71 (s, 3 H), 4.88 (dt, J = 9 and 6 Hz, 1 H), 6.51 (br d, J = 9 Hz, 1 H). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.64; H, 8.72; N, 8.81.

***N*-(Methoxycarbonyl)-α-propylpiperidine (1c)** was prepared by the $TiCl_4$-catalyzed reaction of α-methoxy-*N*-(methoxycarbonyl)piperidine with allyltrimethylsilane followed by hydrogenation in 82% yield or by the reaction of α-methoxy-*N*-(methoxycarbonyl)piperidine with propylmagnesium bromide in the presence of $BF_3{\cdot}O(C_2H_5)_2$ in 45% yield:[22] IR (neat) 2935, 2865, 1685, 1445, 1370, 1260, 1180, 1148, 1090, 767 cm^{-1}; NMR (CCl_4) δ 0.93 (t, J = 6 Hz, 3 H), 1.10–1.92 (m, 10 H), 2.78 (dt, J = 12 and 3 Hz, 1 H), 3.60 (s, 3 H), 3.81–4.40 (m, 2 H). Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.96; H, 10.64; N, 7.58.

Anodic Oxidation of 1a–d in AcOH Containing AcOK. A general procedure for α,β-diacetoxylation of **1a–d** is exemplified by the anodic oxidation of **1a**. Into an electrolysis cell as described above was added a solution of **1a** (2.145 g, 15 mmol) and AcOK (3.0 g, 30.6 mmol) in acetic acid (30 mL). After 12 faradays/mol of electricity was passed at a constant current of 0.4 A (12 h, terminal voltage; ca. 35 V) through the solution cooled with water, aqueous $NaHCO_3$ was added into the reaction mixture cooled with ice–water (method b in Table I, run 2), and the organic portion was extracted with CH_2Cl_2 (30 mL × 4). After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel ($AcOC_2H_5$:hexane = 1:1) to afford **α,β-diacetoxy-*N*-(methoxycarbonyl)piperidine (2a)** in 61% yield and **β-acetoxy-α-hydroxy-*N*-(methoxycarbonyl)piperidine (3a)** in 20% yield.

On the other hand, working up the reaction mixture by stirring with water at room temperature for 6 h (method a in Table I, run 1) afforded only **3a** in 88% yield (20 faradays/mol).

2a: IR (neat) 2953, 2880, 1740, 1708, 1442, 1368, 1238, 1222, 1160, 1044, 769 cm^{-1}; NMR (CCl_4) δ 1.42–1.98 (m, 4 H), 1.91 (s, 3 H), 2.02 (s, 3 H), 2.60–3.33 (m, 1 H), 3.61–4.13 (m, 1 H), 3.68 (s, 3 H), 4.51–4.91 (m, 1 H), 6.31 and 6.71 (2 d, J = 4 and 6 Hz, $^1/_3$ H and $^2/_3$ H). Anal. Calcd for $C_{11}H_{17}NO_6$: C, 50.96; H, 6.61; N, 5.40. Found: C, 51.10; H, 6.87; N, 5.40.

3a: IR (neat) 3440, 2953, 2865, 1738, 1698, 1450, 1367, 1242, 1155, 1052, 1002, 775 cm^{-1}; NMR (CCl_4) δ 1.23–2.00 (m, 4 H), 2.03 (s, 3 H), 2.86–3.33 (m, 1 H), 3.66 (s, 3 H), 3.60–3.93 (m, 1 H), 4.43–5.30 (m, 2 H), 5.47 and 5.70 (2 d, J = 3 and 4 Hz, $^1/_2$ H and $^1/_2$ H). Anal. Calcd for $C_9H_{15}NO_5$: C, 49.76; H, 6.96; N, 6.45. Found: C, 49.47; H, 6.97; N, 6.31.

Similarly, the anodic oxidation (20 faradays/mol of electricity) of **1b** followed by the workup (method b in Table I, run 4) gave **2b** and **3b** in 34 and 45% yields, respectively, while the workup (method a in Table I, run 3) gave only **3b** in 92% yield. Similar anodic oxidation of **1c,d** gave **3c,d**.

α,β-Diacetoxy-*N*-(methoxycarbonyl)-α′-methylpiperidine (2b): IR (neat) 2955, 1746, 1718, 1445, 1372, 1315, 1240, 1208, 785 cm^{-1}; NMR (CCl_4) δ 1.03–2.27 (m, 4 H), 1.18 (d, J = 6 Hz, 3 H), 1.95, 2.03, and 2.07 (3 s, 6 H), 3.77 (s, 3 H), 4.06–4.51 (m, 1 H), 4.70–4.91 (m, 1 H), 6.46 and 6.76 (2 d, J = 1 and 3 Hz, $^1/_4$ H and $^3/_4$ H). Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.98; H, 7.23; N, 5.17.

β-Acetoxy-α-hydroxy-*N*-(methoxycarbonyl)-α′-methylpiperidine (3b): IR (neat) 3450, 2965, 1740, 1702, 1688, 1456, 1375, 1242, 1034, 780 cm^{-1}; NMR (CCl_4) δ 1.15–2.27 (m, 4 H), 1.27 (d, J = 8 Hz, 3 H), 2.02 (s, 3 H), 3.68 (s, 3 H), 3.96–4.38 (m, 2 H), 4.62–4.90 (m, 1 H), 5.40 and 5.60 (2 d, J = 3 and 4 Hz, $^1/_6$ H and $^5/_6$ H); mass spectrum, m/e 214 (M^+ – OH), 171 (100%, M^+ – AcOH); exact mass calcd m/e 214.1080 (M – OH), found 214.0180 (M^+ – OH).

β-Acetoxy-α-hydroxy-*N*-(methoxycarbonyl)-α′-propylpiperidine (3c): 93% yield at 21 faradays/mol (method a in Table I, run 5); IR (neat) 3430, 2970, 2880, 1740, 1712, 1456, 1240, 1052, 778 cm^{-1}; NMR (CCl_4) δ 0.93 (t, J = 7 Hz, 3 H), 0.99–2.30 (m, 8 H), 2.03 (s, 3 H), 3.53–4.24 (m, 1 H), 3.68 (s, 3 H), 4.41–4.90 (m, 1 H), 5.43 and 5.67 (2 d, J = 3 and 4 Hz, $^1/_4$ H and $^3/_4$ H), 6.13 (br s, 1 H); mass spectrum, m/e 242 (M^+ – OH), 198 (100%, M^+ – AcOH), 156. Anal. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.34; H, 8.33; N, 5.41.

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α'-Acetonyl-β-acetoxy-α-hydroxy-N-(methoxycarbonyl)-piperidine (3d): 53% yield at 18 faradays/mol (method a in Table I, run 6); IR (neat) 3400, 2950, 2865, 1740, 1680, 1452, 1378, 1246, 1030, 790 cm^{-1}; NMR (CCl_4) δ 1.20–2.24 (m, 4 H), 2.01 (s, 3 H), 2.11 (s, 3 H), 2.77 (d, J = 6 Hz, 2 H), 3.64 (br s, 1 H), 3.66 (s, 3 H), 4.28–4.87 (m, 2 H), 5.42 and 5.66 (2 d, J = 3 and 4 Hz, $^1/_6$ H and $^5/_6$ H); mass spectrum, m/e 273 (M^+), 256 (M^+ – OH), 212, 198, 172, 156, 154, 141, 138 (100%); exact mass calcd m/e 273.1211, found 273.1190. Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.64; H, 6.95; N, 4.85.

Anodic Oxidation of 1a,b and 5a,b in Aqueous CH_3CN Containing NH_4Cl. α-Hydroxy-β-chlorination of **1a,b** and **5a,b** in aqueous acetonitrile was carried out under the following conditions. Into an electrolysis cell as described above was added a solution of **1a** (0.429 g, 3 mmol) and NH_4Cl (2.0 g, 37.4 mmol) in acetonitrile (30 mL) and water (3 mL). After 15 faradays/mol of electricity was passed at a constant current of 0.5 A (2.4 h, terminal voltage; ca. 45 V) through the solution, water (30 mL) was added to the electrolyzed solution and the organic portion was extracted with CH_2Cl_2 (25 mL × 4). After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel ($AcOC_2H_5$:hexane = 1:1) to afford **β-chloro-α-hydroxy-N-(methoxycarbonyl)-piperidine (4a)** in 57% yield. By the similar procedure were obtained **4b** and **6a,b** from **1b** and **5a,b**, respectively.

4a: IR (neat) 3360, 2954, 2860, 1700, 1680, 1444, 1260, 1037, 768 cm^{-1}; NMR (CCl_4) δ 1.26–2.62 (m, 4 H), 2.86–3.43 (m, 1 H), 3.53–4.47 (m, 3 H), 3.73 (s, 3 H), 5.60–5.99 (br s, 1 H); mass spectrum, m/e 192 (M^+ – H), 158 (M^+ – Cl), 157 (M^+ – HCl), 140, 103, 88 (100%); exact mass calcd m/e 192.0426 (M – H), found 192.0419 (M^+ – H). Anal. Calcd for $C_7H_{12}NO_3Cl$: C, 43.42; H, 6.25; N, 7.23; Cl, 18.31. Found: C, 43.52; H, 6.27; N, 7.17; Cl, 18.46.

β-Chloro-α-hydroxy-N-(methoxycarbonyl)-α'-methyl-piperidine (4b): 47% yield at 15 faradays/mol; IR (neat) 3400, 2950, 1708, 1442, 1090, 975, 788, 732 cm^{-1}; NMR (CCl_4) δ 1.15 (d, J = 7 Hz, 3 H), 1.43–1.77 (m, 2 H), 1.90–2.49 (m, 2 H), 3.31 (br s, 1 H), 3.79 (s, 3 H), 4.05–4.56 (m, 2 H), 5.90 (br s, 1 H); mass spectrum, m/e 209 (M^+ + 2), 207 (M^+), 194 (M^+ + 2 – OH), 192 (100%, M^+ – OH), 154; exact mass calcd m/e 207.0662, found 207.0648.

β-Chloro-α-hydroxy-N-(methoxycarbonyl)pyrrolidine (6a): 47% yield at 20 faradays/mol; mp 60–61 °C (from ether); IR (neat) 3500, 2968, 2905, 1692, 1458, 1387, 1208, 1126, 1030, 778 cm^{-1}; NMR ($CDCl_3$) δ 1.84–2.85 (m, 2 H), 3.49 (br d, J = 4 Hz, 1 H), 3.63 (br s, 1 H), 3.72 (s, 3 H), 4.17 (br d, J = 4 Hz, 1 H), 5.21 (br s, 1 H), 5.39 (br s, 1 H); mass spectrum, m/e 181 (M^+ + 2), 179 (M^+), 164 (M^+ + 2 – OH), 162 (M^+ – OH), 144 (M^+ – Cl), 117 (100%); exact mass calcd m/e 179.0350, found 179.0362. Anal. Calcd for $C_6H_{10}NO_3Cl$: C, 40.12; H, 5.61; N, 7.80; Cl, 19.74. Found: C, 40.07; H, 5.65; N, 8.00; Cl, 19.53.

β-Chloro-α',N-bis(methoxycarbonyl)-α-hydroxy-pyrrolidine (6b): 68% yield at 50 faradays/mol; IR (neat) 3450, 2975, 1730, 1705, 1459, 1383, 1208, 1137, 1052, 1020, 780 cm^{-1}; NMR (CCl_4) δ 2.13–2.93 (m, 2 H), 3.81 (s, 3 H), 3.86 (s, 3 H), 4.12–5.40 (m, 3 H), 5.67 (br s, 1 H); mass spectrum, m/e 220 (M^+ – OH), 202 (M^+ – Cl), 201 (M^+ – HCl), 180 (M^+ + 2 – CO_3CH_3), 178 (100%, M^+ – CO_2CH_3), 143 (M^+ – Cl – CO_2CH_3). Anal. Calcd for $C_8H_{12}NO_5Cl$: C, 40.43; H, 5.09; N, 5.89; Cl, 14.92. Found: C, 40.41; H, 5.36; N, 5.66; Cl, 14.71.

Anodic Oxidation of 1a,b in CH_2Cl_2 Containing $(C_2H_5)_4NOTs$. Into an electrolysis cell as described above were added a solution of **1a** (0.429 g, 3.0 mmol) and $(C_2H_5)_4NOTs$ (0.15 g, 0.5 mmol) in CH_2Cl_2 (10 mL). After 5 faradays/mol of electricity was passed at a constant current of 0.3 A (1.4 h, terminal voltage; ca. 30 V) through the solution, the usual workup gave **4a** in 31% yield. Similarly, **4b** was obtained from **1b** in 61% yield (11.2 faradays/mol).

Anodic Oxidation of 1a in CH_3OH Containing NH_4Cl. Into an electrolysis cell as described above was added a solution of **1a** (2.145 g, 15 mmol) and NH_4Cl (1.17 g, 21.9 mmol) in methanol (40 mL), and 15 faradays/mol of electricity was passed at a constant current of 1 A (6.4 h, terminal voltage; ca. 12 V) through the solution. After the solvent was removed in vacuo without heating, water (30 mL) was added to the residue, and the organic portion was extracted with CH_2Cl_2 (25 mL × 4). After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel ($AcOC_2H_5$:hexane = 1:5) to afford **β-chloro-α-methoxy-N-(methoxycarbonyl)-piperidine (7)** in 90% yield.

7: IR (neat) 2970, 1710, 1452, 1279, 1182, 1085, 965, 949, 774, 706 cm^{-1}; NMR (CCl_4) δ 1.24–2.32 (m, 4 H), 2.91 (br t, J = 12 Hz, 1 H), 3.29 and 3.35 (2 s, $^{12}/_5$ H and $^3/_5$ H), 3.60–4.21 (m, 2 H), 3.72 (s, 3 H), 5.31 (br s, 1 H); mass spectrum, m/e 209 (M^+ + 2), 207 (M^+), 178 (M^+ + 2 – OCH_3), 176 (100%, M^+ – OCH_3); exact mass calcd m/e 207.0663, found 207.0687. Anal. Calcd for $C_8H_{14}NO_3Cl$: C, 46.27; H, 6.80; N, 6.75; Cl, 17.07. Found: C, 46.74; H, 7.04; N, 6.69; Cl, 16.67.

Anodic Oxidation of 8a–e in AcOH. α,β-Diacetoxylation of **8a–e** was achieved under conditions similar to the anodic oxidation of **1a–d** in acetic acid. After the workup (method b), products were isolated by column chromatography (silica gel). The yields of **2a** and **3a** were 65 and 22% yields (6 faradays/mol), respectively.

α,β-Diacetoxy-N-(methoxycarbonyl)pyrrolidine (9b): 55% yield at 3.8 faradays/mol; IR (neat) 2954, 1720, 1448, 1392, 1240, 1206, 1018, 952, 775 cm^{-1}; NMR (CCl_4) δ 1.83–2.23 (m, 2 H), 2.01 (s, 3 H), 2.06 (s, 3 H), 3.23–3.60 (m, 2 H), 3.67 (s, 3 H), 4.86–5.10 (m, 1 H), 6.21–6.77 (m, 1 H); mass spectrum, m/e 202 (M^+ – Ac), 186 (M^+ – OAc), 173, 160, 143 (100%, M^+ – OAc – Ac); exact mass calcd m/e 202.0715 (M – Ac), found 202.0713 (M^+ – Ac).

N-(α,β-Diacetoxybutyl)-N-(methoxycarbonyl)butylamine (9c): 76% yield at 4.2 faradays/mol; IR (neat) 2952, 2876, 1732, 1695, 1452, 1370, 1218, 1018, 775 cm^{-1}; NMR (CCl_4) δ 0.80–1.08 (m, 6 H), 1.12–1.76 (m, 6 H), 1.99 (s, 3 H), 2.01 (s, 3 H), 3.00–3.04 (m, 2 H), 3.70 and 3.72 (2 s, 3 H), 4.97–5.26 (m, 1 H), 6.39 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{14}H_{25}NO_6$: C, 55.43; H, 8.31; N, 4.62. Found: C, 55.39; H, 8.53; N, 4.78.

N-(α,β-Diacetoxybutyl)-N-(methoxycarbonyl)allylamine (9d): 83% yield at 5.9 faradays/mol; IR (neat) 3080, 2972, 2880, 1732, 1705, 1450, 1370, 1312, 1220, 1020, 772 cm^{-1}; NMR (CCl_4) δ 0.85 and 0.90 (2 t, J = 9 and 9 Hz, 3 H), 1.24–1.80 (m, 2 H), 1.95 (s, 3 H), 1.98 (s, 3 H), 3.67 (s, 3 H), 3.71–3.88 (m, 2 H), 4.90–5.30 (m, 3 H), 5.51–6.03 (m, 1 H), 6.34 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{13}H_{21}NO_6$: C, 54.34; H, 7.37; N, 4.88. Found: C, 54.20; H, 7.42; N, 4.85.

α,β-Diacetoxy-α',N-bis(methoxycarbonyl)piperidine (9e): 75% yield at 7 faradays/mol; IR (neat) 2975, 1740, 1452, 1378, 1205, 1030, 1018 cm^{-1}; NMR (CCl_4) δ 1.64–2.35 (m, 4 H), 2.03 (s, 3 H), 2.10 (s, 3 H), 3.77 (s, 3 H), 3.84 (s, 3 H), 4.91 (br s, 2 H), 6.63–6.84 (m, 1 H). Anal. Calcd for $C_{13}H_{19}NO_8$: C, 49.21; H, 6.04; N, 4.41. Found: C, 48.94; H, 6.15; N, 4.11.

α-Hydroxy- or α-Methoxy-β-chlorination of 8a. Compound **8a** was transformed to **4a** by the anodic oxidation similar to that of **1a** in aqueous acetonitrile containing NH_4Cl (79% yield at 3.5 faradays/mol) or in CH_2Cl_2 containing $(C_2H_5)_4NOTs$ (34% yield at 6 faradays/mol). Compound **7** was obtained from **8a** by the similar anodic oxidation of **1a** in methanol containing NH_4Cl (82% yield at 6 faradays/mol).

Transformation of 8a to 7 with t-C_4H_9OCl in CH_3OH. Into a solution of **8a** (2.822 g, 20 mmol) in methanol (30 mL) at room temperature was added dropwise *tert*-butyl hypochlorite (2.98 mL, 25 mmol) in a period of 2 min. After the solution was stirred for 10 min, the usual workup afforded **7** in 70% yield. The ^1H NMR spectrum of **7** obtained by this method was identical with that of **7** obtained by anodic oxidation of **1a**.

Anodic Oxidation of 8a,b,f in CH_3OH Containing NH_4X or NaX. α-Methoxy-β-bromination and -β-iodination of **8a,b,f** in methanol were carried out by the procedures as exemplified by β-bromination of **8b**. Into an electrolysis cell as described above was added a solution of **8b** (0.636 g, 5 mmol) and NH_4Br (0.735 g, 7.5 mmol) in methanol (20 mL), and 3.5 faradays/mol of electricity was passed at a constant current of 0.3 A (1 h, terminal voltage; ca. 6 V) through the solution. After the solvent was removed in vacuo without heating, aqueous $Na_2S_2O_3$ (20 mL) was added to the residue, and the organic portion was extracted with CH_2Cl_2 (15 mL × 4). After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel ($AcOC_2H_5$:hexane = 1:5) to afford **β-bromo-α-methoxy-N-(methoxycarbonyl)pyrrolidine (10p)** in 42% yield.

Compounds **10q**, **11p,q**, and **12p,q** were obtained according to the similar procedures.

10p: IR (neat) 2955, 1718, 1450, 1200, 1180, 1122, 1080, 778 cm^{-1}; NMR (CCl_4) δ 1.93–2.84 (m, 2 H), 3.26–3.84 (m, 2 H), 3.39 (s, 3 H), 3.74 (s, 3 H), 4.16 (br d, J = 5 Hz, 1 H), 5.09–5.34 (m, 1 H). Anal. Calcd for $C_7H_{12}NO_3Br$: C, 35.31; H, 5.08; N, 5.88; Br, 33.56. Found: C, 35.52; H, 5.07; N, 5.59; Br, 33.81.

β-Iodo-α-methoxy-*N*-(methoxycarbonyl)pyrrolidine (10q): 38% yield at 5.0 faradays/mol (supporting electrolyte NH_4I); IR (neat) 2960, 1715, 1452, 1380, 1112, 1080, 958, 780 cm^{-1}; NMR (CCl_4) δ 2.03–2.81 (m, 2 H), 3.20–3.80 (m, 2 H), 3.34 (br s, 3 H), 3.74 (s, 3 H), 4.16 (br d, J = 5 Hz, 1 H), 5.16–5.43 (m, 1 H). Anal. Calcd for $C_7H_{12}NO_3I$: C, 29.49; H, 4.24; N, 4.91; I, 44.52. Found: C, 29.67; H, 4.30; N, 4.97; I, 44.52.

β-Bromo-α-methoxy-*N*-(methoxycarbonyl)piperidine (11p): 81% yield at 3.5 faradays/mol (supporting electrolyte NaBr); IR (neat) 2952, 1708, 1448, 1272, 1160, 1082, 968, 952, 778 cm^{-1}; NMR (CCl_4) δ 1.29–2.45 (m, 4 H), 2.95 (br t, J = 12 Hz, 1 H), 3.27 and 3.36 (2 s, $^5/_2$ H and $^1/_2$ H), 3.63–4.63 (m, 2 H), 3.74 (s, 3 H), 5.44 (br s, 1 H); mass spectrum, m/e 253 (M^+ + 2), 251 (M^+), 222 ($M^+ - OCH_3 + 2$), 220 (100%, $M^+ - OCH_3$); exact mass calcd m/e 251.0157, found 251.0146.

β-Iodo-α-methoxy-*N*-(methoxycarbonyl)piperidine (11q): 81% yield at 4.0 faradays/mol (supporting electrolyte NaI); IR (neat) 2950, 1712, 1448, 1258, 1200, 1152, 1072, 940 cm^{-1}; NMR (CCl_4) δ 1.34–2.24 (m, 4 H), 2.97 (br t, J = 12 Hz, 1 H), 3.26 (s, 3 H), 3.75 (s, 3 H), 3.79–4.14 (m, 1 H), 4.41 (br s, 1 H), 5.44 (br s, 1 H); mass spectrum, m/e 268 ($M^+ - OCH_3$), 172 (M^+ - I), 158 (100%); exact mass calcd m/e 267.9837 (M - OCH_3), found 267.9856 ($M^+ - OCH_3$).

β-Bromo-α-methoxy-*N*-(methoxycarbonyl)azacycloheptane (12p): 70% yield at 5.0 faradays/mol (supporting electrolyte: NaBr); IR (neat) 2948, 2855, 1703, 1438, 1335, 1118, 1095, 1085, 1010, 955, 776 cm^{-1}; NMR (CCl_4) δ 1.13–2.31 (m, 6 H), 2.59–3.96 (m, 3 H), 3.28 (s, 3 H), 3.74 (s, 3 H), 5.25–5.61 (m, 1 H); mass spectrum, m/e 267 (M^+ + 2), 265 (M^+), 236 ($M^+ + 2 - OCH_3$), 234 ($M^+ - OCH_3$), 208, 206, 186 (M^+ - Br), 154, 144, 128 (100%); exact mass calcd m/e 265.0314, found 265.0302.

β-Iodo-α-methoxy-*N*-(methoxycarbonyl)azacycloheptane (12q): 66% yield at 4.5 faradays/mol (supporting electrolyte NaI); IR (neat) 2940, 2850, 1700, 1436, 1338, 1137, 1105, 1088, 1068, 1003, 943, 770 cm^{-1}; NMR (CCl_4) δ 1.23–2.51 (m, 6 H), 2.69–3.09 (m, 1 H), 3.18–4.13 (m, 2 H), 3.32 (s, 3 H), 3.79 (s, 3 H), 5.36–5.73 (m, 1 H); mass spectrum, m/e 313 (M^+), 282 ($M^+ - OCH_3$), 254, 196, 186 (100%, M^+ - I); exact mass calcd m/e 313.0176, found 313.0151.

Reduction of 4a and 9b. A general procedure is exemplified by reduction of **9b**. Into a solution of **9b** (0.238 g, 0.97 mmol) in acetic acid (4 mL) was added in portions 90% $NaBH_4$ (0.184 g, 4.36 mmol). After 1.5 h, aqueous $NaHCO_3$ (60 mL) was poured into the reaction mixture and the organic portion was extracted with CH_2Cl_2 (20 mL × 4). After the extract was dried over $MgSO_4$ and the solvent was removed in vacuo, the residue was chromatographed on silica gel ($AcOC_2H_5$:hexane = 1:2) to afford **β-acetoxy-*N*-(methoxycarbonyl)pyrrolidine (13)** in 82% yield.

13: IR (neat) 2955, 2890, 1741, 1710, 1458, 1395, 1248, 1202, 775 cm^{-1}; NMR (CCl_4) δ 1.83–2.29 (m, 2 H), 2.07 (s, 3 H), 3.09–3.84 (m, 4 H), 3.66 (s, 3 H), 5.15–5.49 (m, 1 H); mass spectrum, m/e 127 (100%, M^+ - AcOH). Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.05; H, 6.99; N, 7.20.

The reduction of **4a** under the similar conditions gave **14**.

β-Chloro-*N*-(methoxycarbonyl)piperidine (14): 80% yield from **4a**; IR (neat) 2972, 2880, 1718, 1481, 1454, 1419, 1270, 1248, 1202, 1162, 1138, 972, 778, 770 cm^{-1}; NMR (CCl_4) δ 1.23–2.49 (m, 4 H), 2.76–3.30 (m, 2 H), 3.53–4.30 (m, 3 H), 3.68 (s, 3 H); mass spectrum, m/e 179 (M^+ + 2), 177 (M^+), 164, 162, 142 (M^+ - Cl), 102 (100%); exact mass calcd m/e 177.0556, found 177.0543.

Transformation of 6a and 11p to 15 and 16. A mixture of **6a** (0.332 g, 1.85 mmol) and NH_4Cl (0.01 g, 0.19 mmol) was heated (100 °C) under an atmosphere of nitrogen with reduced pressure (22 mm) for 3 h. After the reaction was completed, **β-chloro-α,β-didehydro-*N*-(methoxycarbonyl)pyrrolidine (15)** was isolated by Kugelrohr distillation in 94% yield. **β-Bromo-α,β-didehydro-*N*-(methoxycarbonyl)piperidine (16)** was prepared in 96% yield by heating (225 °C) **12p** under reduced pressure (45 mm).

15: bp 140 °C (22 mm); IR (neat) 2970, 2915, 1718, 1459, 1390, 1200, 1132 cm^{-1}; NMR (CCl_4) δ 2.85 (br t, J = 10 Hz, 2 H), 3.73 (s, 3 H), 3.87 (br t, J = 10 Hz, 2 H), 6.62 (br s, 1 H); mass spectrum, m/e 163 (M^+ + 2), 161 (100%, M^+); exact mass calcd m/e 161.0244, found 161.0250.

16: bp 225 °C (42 mm); IR (neat) 3100, 2950, 1708, 1654, 1440, 1382, 1342, 1302, 1250, 1190, 1120, 982, 968, 762, 748 cm^{-1}; NMR (CCl_4) δ 1.97 (tt, J = 6 and 6 Hz, 2 H), 2.46 (t, J = 6 Hz, 2 H), 3.59 (t, J = 6 Hz, 2 H), 3.75 (s, 3 H), 7.12 (br s, 1 H). Anal. Calcd for $C_7H_{10}NO_2Br$: C, 38.21; H, 4.58; N, 6.36; Br, 36.31. Found: C, 38.31; H, 4.56; N, 6.19; Br, 36.04.

Oxidation Potentials. Oxidation potentials were measured at room temperature by using an H-type cell, potentiostat HA-104, and function generator HB-107A (Hokuto Denko Ltd.). Oxidation was carried out in dry acetonitrile containing 0.1 N $LiClO_4$ as a supporting electrolyte at platinum electrode using an aqueous saturated calomel reference electrode. The scan rate was 100 mV/s. The concentrations of **8a** and **8b** were 4 mmol/L.

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Synthesis and Alkali-Metal Complexing Abilities of Crown Ether Tertiary Alcohols

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Twenty-three crown ethers with a hydroxyl and an alkyl or aryl group linked directly to the central carbon of a three-carbon bridge were synthesized in one-step reactions of glycol and bisphenol dianions with substituted 2-(chloromethyl)oxiranes. Crown ether tertiary alcohols with methyl, *n*-decyl, *n*-tetradecyl, phenyl, and *p*-(*n*-decyl)phenyl substituents and four ring sizes are prepared. The effect of substituent on Na^+ and K^+ complexation is assessed by the picrate extraction method for closely related tertiary crown ether alcohols with 16-crown-5 and 15-crown-5 rings.

Crown ether alcohols are versatile synthetic intermediates for the preparation of ionophores with pendant arms,[1] bis crowns,[2] and polymer-bound crowns.[3] Pendant arms with additional neutral or anionic coordination sites often provide substantially increased metal ion binding

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