Oxidation Potential. For the polarographic investigation, Yanagimoto P8-DP type three-electrode polarograph equipped with rotating platinum electrode (1000 rpm) was used. Anhydrous lithium perchlorate was dried without further purification at 150° for 12 hr. Acetonitrile was distilled three times over phosphorus pentoxide. Substrate was dissolved in acetonitrile in a concentration of 0.67 mmol. 4-Substituted [2.2]paracyclophanes were synthesized by the authentic method.[13]

References and Notes

(1) A part of this work was previously reported in preliminary letters: T. Shono, A. Ikeda, and S. Hakozaki, *Tetrahedron Lett.*, 4511 (1972).
(2) T. Shono and A. Ikeda, *J. Am. Chem. Soc.*, **94**, 7892 (1972).
(3) T. Shono, A. Ikeda, and Y. Kimura, *Tetrahedron Lett.*, 3599 (1971).
(4) I. Tabushi, K. Fujita, and R. Oda, *J. Org. Chem.*, **35**, 2376 (1970).
(5) J. B. Lambert and A. C. Holcomb, *J. Am. Chem. Soc.*, **93**, 2994 (1971).
(6) (a) A. Gagneux and C. A. Grob, *Helv. Chem. Acta*, **42**, 2006 (1959); (b) G. A. Grob and J. Hostynek, *ibid.*, **46**, 1676 (1963); (c) P. Brown and R. C. Cookson, *Tetrahedron*, **24**, 2551 (1968).
(7) S. Moon and C. R. Ganz, *J. Org. Chem.*, **35**, 1214 (1970).
(8) The interaction between nonconjugated double bonds in the cathodic reduction has been studied in some systems.[9]
(9) J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, **31**, 3897 (1966); D. A. Tyssee, J. H. Wagenknecht, M. M. Baizer, and J. L. Chruma, *Tetrahedron Lett.*, 4809 (1972).
(10) W. C. Baied and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968).
(11) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968).
(12) (a) J. A. Berson, D. S. Donald, and W. J. Libbey, *J. Am. Chem. Soc.*, **91**, 5580 (1969); (b) J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, *J. Org. Chem.*, **36**, 510 (1971).
(13) (a) H. E. Weinberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960); (b) D. J. Cram and N. L. Allinger, *ibid.* **77**, 6289 (1955).

Electroorganic Chemistry. XX.[1] Anodic Oxidation of Carbamates

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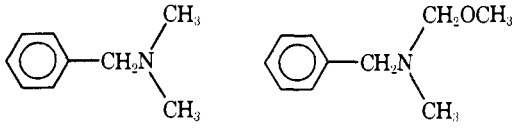
Abstract: The anodic oxidation of methyl *N,N*-dialkylcarbamate (**4**) in methanol yielded three types of products, that is, α-methoxylated compound (**5**), enamine-type product (**6**) and dealkylated carbamate (**7**). Inter- and intramolecular isotope effects were measured to be 1.5–1.6 and 1.8–1.9, respectively. The reaction mechanism was discussed on the bases of product study, oxidation potential of carbamate, current-potential relationship, and isotope effect, and the electron transfer from the carbamate to anode was suggested as the initiation process.

The anodic oxidation of *N*-alkyl aromatic amines in methanol has been shown to give α-methoxylated products,[2] whereas the reaction of aliphatic amines yields dealkylated products.[3] It is of much interest in these reactions that the regioselectivity of the substitution or the direction of the elimination is hardly predictable on the basis of the hitherto known behaviors of the radical and cation.

For example, *N,N*-dimethylbenzylamine (**1**) yielded *N*-methoxymethyl-*N*-methylbenzylamine (**2**) rather than



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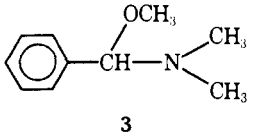

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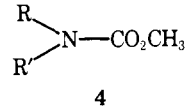
N,N-dimethyl-α-methoxybenzylamine (**3**). Weinberg et al.[2,4] explained this unusual behavior in terms of the stereochemistry of the adsorption of the intermediate cation radical on the anode, although this explanation was not always sufficient.[5]

In another case, diisopropylethylamine resulted in the preferential loss of ethyl group.[6] Mann et al. suggested the possibility of the intervention of an enamine intermediate in the dealkylation step.

In the present study, the anodic oxidation of methyl *N,N*-dialkylcarbamate (**4**) was mechanistically scrutinized



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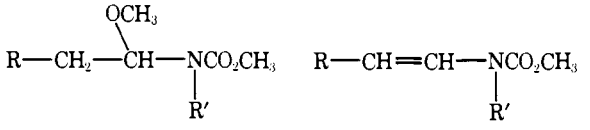
R, R′ = H, Me, *n*- and *i*-Pr, *n*-Bu, cyclohexyl, $C_6H_5CH_2$, $-(CH_2)_4-$, $-(CH_2)_5-$

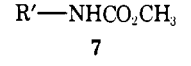
to clarify the rather peculiar chemical behavior of the amine derivatives in the electrochemical oxidation.

Results

Product Study. All anodic oxidations of methyl *N*-alkyl-substituted carbamates were carried out in methanol at room temperature using tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte. The products consisted of three types of compounds, that is, α-methoxylated compounds (**5**), enamine type product (**6**), and dealkylated car-



5 **6**



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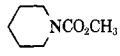
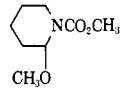
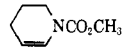
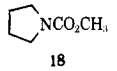
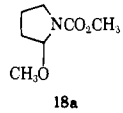
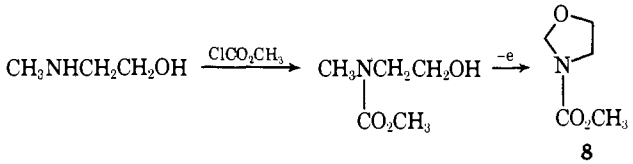
bamate (**7**). The results are summarized in Table I. Furthermore, this anodic reaction was utilized in the synthesis of oxazoline derivatives, the yield of **8** being 60%.

Table I. Anodic Oxidation of Carbamate

Carbamate	Anode potential (V vs. SCE)	Product	Yield,[a] %
$CH_3CH_2CH_2NHCO_2CH_3$ **15**	1.65	$CH_3CH_2C(OCH_3)HNHCO_2CH_3$ **15a**	62
$(CH_3CH_2CH_2)_2NCO_2CH_3$ **16**	1.80	$CH_3CH_2CH_2NHCO_2CH_3$ **15**	5
		$CH_3CH_2C(OCH_3)H(CH_3CH_2CH_2)NCO_2CH_3$ **16a**	68
$(CH_3CH_2CH_2CH_2)_2NCO_2CH_3$ **17**	2.20	$CH_3CH_2CH_2C(OCH_3)H(CH_3CH_2CH_2CH_2)NCO_2CH_3$ **17a**	63
 **10**	1.75	 **10a**	72
		 **10b**	trace
 **18**	1.80	 **18a**	65
$(CH_3)_2CHNHCO_2CH_3$ **19**	2.12	$NH_2CO_2CH_3$	11
$((CH_3)_2CH)_2NCO_2CH_3$ **20**	1.95	$(CH_3)_2CHNHCO_2CH_3$ **19**	15
$c\text{-}C_6H_{11}NHCO_2CH_2$ **21**	2.21	$NH_2CO_2CH_3$	8
		$c\text{-}C_6H_{10}{=}O$	4
$CH_3CH_2CH_2CH_2(CH_3)NCO_2CH_3$ **22**	1.95	$CH_3CH_2CH_2CH_2(CH_3OCH_2)NCO_2CH_3$ **22a**	53
$c\text{-}C_6H_{11}(CH_3)NCO_2CH_3$ **23**	1.80	$c\text{-}C_6H_{11}(CH_3OCH_2)NCO_2CH_3$ **23a**	78
$C_6H_5CH_2(CH_3)NHCO_2CH_3$ **24**	1.80	$C_6H_5C(OCH_3)H(CH_3)NCO_2CH_3$ **24a**	18
		$C_6H_5CH_2(CH_3OCH_2)NCO_2CH_3$ **24a'**	45
$(CH_3)_3CNHCO_2CH_3$	2.25		0[b]

[a] Isolated chemical yields at the time when 2 Faradays/mol of electricity was passed. [b] The recovery of starting material was 98%.

Oxidation Potential and Current–Potential Relationship. The oxidation potentials of some methyl *N*-alkyl-substituted carbamates in anhydrous acetonitrile containing tetraethylammonium *p*-toluenesulfonate (0.1 *M*) were measured by using a rotating platinum electrode. Results are tabulated in Table II.



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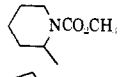
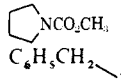
N-Monoalkyl-substituted carbamates, for example, methyl *N*-isopropylcarbamate or methyl *N*-*n*-propylcarbamate, showed no oxidation wave below 2.2 V vs. SCE.

However, the cathodic shift observed in the current–potential relationship (Figure 1) measured as to *N*-carbomethoxypyrrolidine may indicate that the oxidation is initiated by the electron transfer from *N*-carbomethoxypyrrolidine to anode.

Table II. Oxidation Potentials (E_{ox}) of Methyl *N*-Alkyl-Substituted Carbamate

Carbamate	(E_{ox}) (V vs. SCE)
$(CH_3CH_2CH_2CH_2)_2NCO_2CH_3$	1.86
	1.79
	1.73
$C_6H_5CH_2(CH_3)NCO_2CH_3$	1.88
$c\text{-}C_6H_{11}(CH_3)NCO_2CH_3$	1.74

Discussion

Isotope Effect. Two mechanisms would be conceivable for the initiation step of this anodic methoxylation reaction. One of them is the α-hydrogen abstraction by a radical

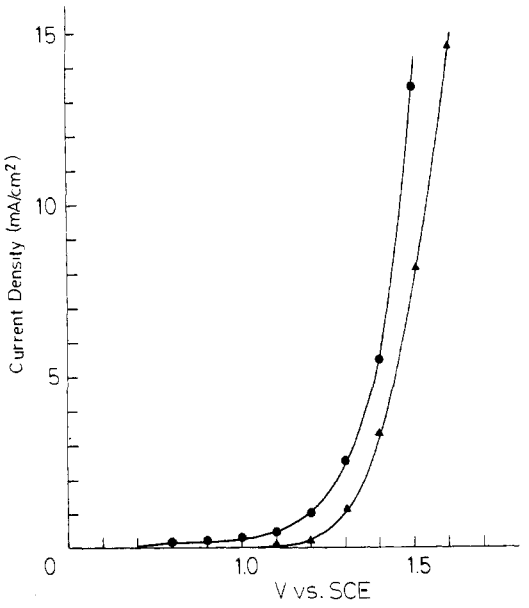
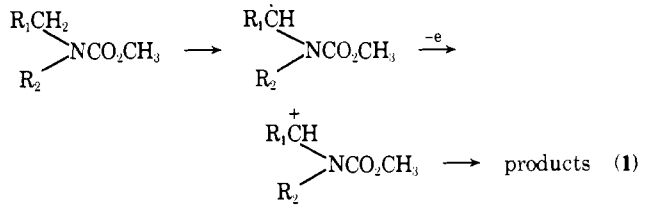


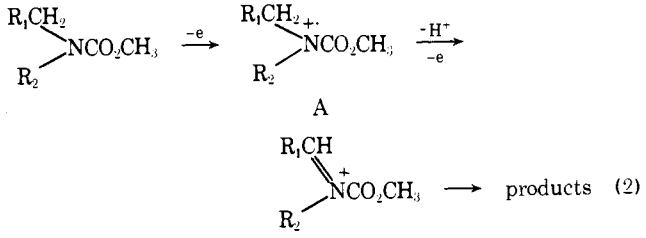
Figure 1. Current-potential relationship: (▲) CH_3OH + Et_4NOTs; (●) CH_3OH + Et_4NOTs + *N*-carbomethoxypyrrolidine (**18**).

species which may be generated from the anodic oxidation of solvent or supporting electrolyte (eq 1) and another is the



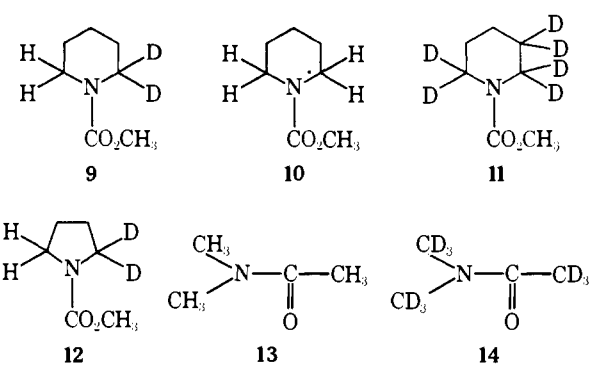
products (1)

electron transfer process (eq 2).



products (2)

An approach for discrimination between (1) and (2) is based on the determination of the isotope effect for this anodic substitution. The isotope effects obtained in the anodic reaction of compounds **9** and **12** are called intramolecular isotope effects, while the effects measured from the competitive reaction of compound **10** and **11**, or **13** and **14** are intermolecular isotope effects. As shown in Table III, the inter- and intramolecular isotope effects obtained by the NMR method[7] were 1.5–1.6 and 1.8–1.9, indicating that the difference between the inter- and intramolecular isotope effects is outside the experimental error.



9 **10** **11**

12 **13** **14**

Table III. Inter- and Intramolecular Isotope Effects[a]

	Intramolecular isotope effect		Intermolecular isotope effect
9	1.81 ± 0.05	10 11	1.59 ± 0.05
12	1.84 ± 0.05	13 14	1.53 ± 0.05

[a] The measurements were carried out at the conversion of 20%.

If the initiation process of this anodic oxidation is the homolytic α-hydrogen abstraction by methoxy radical (mechanism 1), both the inter- and intramolecular isotope effects would be almost identical and the values would be larger than those observed in the present study.[8,9]

On the other hand, if mechanism 2 is operative in the initiation step, the inter- and intramolecular isotope effects would be different and the values would be smaller than those in mechanism 1, because the intramolecular isotope effect is caused by the relative rate of the ejection of a proton or deuterium cation from highly energetic cation radical species A[13], whereas the intermolecular isotope effect is attributable to the small difference[15] in the oxidation potential of each substrate.

The oxidation of some amines by chlorine dioxide has been established to be initiated by electron transfer and the intermolecular isotope effect was 1.3–1.8.[12] All of the above evidences would suggest the agreement of the results shown in Table III with mechanism 2.

Reaction Scheme. On the bases of oxidation potentials, current-potential relationship, and isotope effects, the electron transfer mechanism is suggested for the anodic oxidation of methyl *N*-alkyl-substituted carbamate. Accordingly, the formation of three types of products can reasonably be outlined as shown in Scheme I.

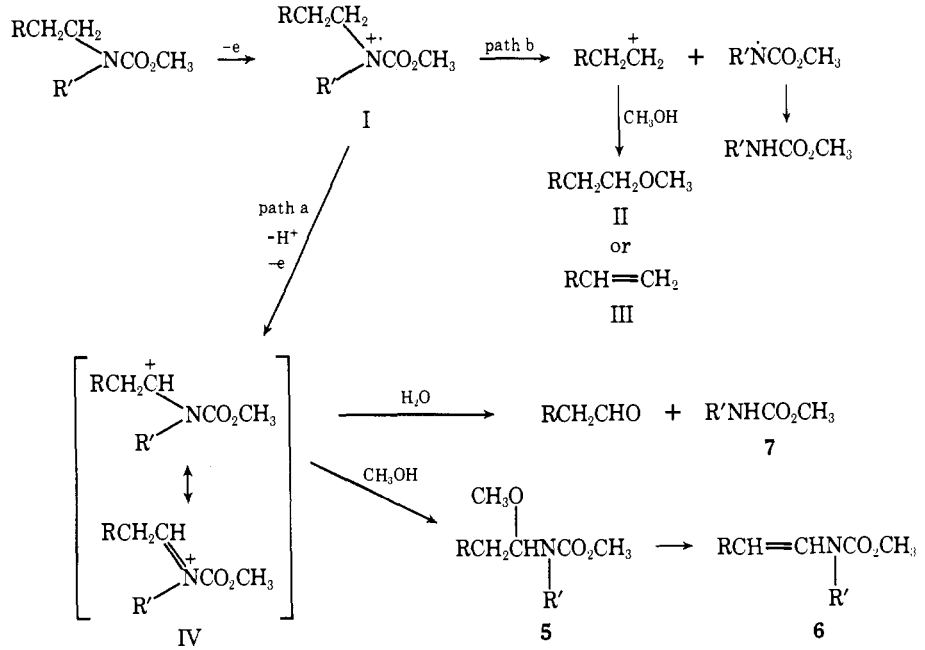
The direct formation of dealkylated product from aminium cation (I) (path b) is ruled out by the fact that ether (II) or olefin (III) was not detected in the reaction products. Enamine type product (**6**) might directly be generated from IV, but the observation of facile conversion of α-methoxy product **5** to **6** under acidic or thermolytic conditions suggested the route shown in Scheme I. The current efficiency increased in the order of methyl *N*-*n*-propylcarbamate > methyl *N*-isopropylcarbamate > methyl *N*-*tert*-butylcarbamate, and the preferential substitution at the methyl group was always observed in methyl *N*-methyl-*N*-*n*-butylcarbamate or methyl *N*-methyl-*N*-cyclohexylcarbamate. These findings may be explicable in terms of the steric factor between the substrate and anode. Ross et al. suggested that the way in which the positive charge densities are distributed on the cation radical is responsible for this unusual behavior[5] and that those positive charge densities can be calculated theoretically.

Experimental Section

Materials. Carbamates were prepared according to the general method[17] from corresponding amines. Dimethylacetamide-d_9 (**14**) was available commercially. Syntheses of compounds **9**, **11**, and **12** were carried out as follows.

Synthesis of *N*-Carbomethoxypiperidine-α,α-d_2 (9). The reduction[18] of δ-valerolactam with $LiAlD_4$ in anhydrous ether gave piperidine-α,α-d_2, which was converted to **9** in an overall yield of 21% by the treatment with methyl chloroformate in aqueous KOH: NMR (CCl_4) τ 6.40 (s, 3, CO_2CH_3), 6.60–6.80 (m, 2, NCH_2), 8.38 (m, 6, CH_2).

Scheme I



Synthesis of *N*-Carbomethoxypiperidine-$\alpha,\alpha,\alpha',\alpha',\beta,\beta$-$d_6$ (11). The Beckmann rearrangement[19] of cyclopentanone oxime-$\alpha,\alpha,\alpha',\alpha'$-$d_4$[20] followed by the reduction with $LiAlD_4$ yielded piperidine-$\alpha,\alpha,\alpha',\alpha',\beta,\beta$-$d_6$ in a yield of 10%, which was converted to **11** by the same method as described in the synthesis of **9**: NMR (CCl_4) τ 6.40 (s, 3, CO_2CH_3), 8.38 (m, 4, CH_2).

Synthesis of *N*-Carbomethoxypyrrolidine-α,α-d_2 (12). α-Pyrrolidone was reduced and converted to **12** in a yield of 17% in the same way as in the preparation of **9**: NMR (CCl_4) τ 6.40 (s, 3, CO_2CH_3), 6.50-6.75 (m, 2, NCH_2), 8.34 (m, 4, CH_2).

Electrochemical Oxidation of Carbamates. General. The preparative electrolyses were carried out according to the following procedure. Into a 50 ml electrolysis cell fitted with two carbon electrodes were placed 0.05 mol of carbamate and 0.005 mol of tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) as electrolyte and 32.04 ml of methanol as a solvent. The constant current (0.5 A) was passed through the cell which was externally cooled with water. After 2 Faradays/mol of electricity was passed, 50 ml of water was added to the reaction mixture and it was extracted with three portions of ether. The combined organic layer was dried on magnesium sulfate overnight. After removing the magnesium sulfate by filtration, the ether was distilled off and the residue was distilled. All products were purified by GLC and identified with spectroscopic methods and elemental analyses, and/or by comparison with authentic samples.

Electrolysis of 15 gave 15a. Yield was shown in Table I. **15a:** bp 70° (3 mm); ir 3300 (N-H), 2840 (methoxy), 1700, 1250 cm^{-1} (ester); NMR (CCl_4) τ 4.50 (broad s, 1, NH), 5.27 (broad s, 1, N-CH-O), 6.33 (s, 3, CO_2CH_3), 6.67 (s, 3, methoxy), 8.15-8.5 (m, 2), 9.00 (t, 3, CH_3). Anal. Calcd for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52. Found: C, 48.73; H, 9.20; N, 9.28.

Electrolysis of 16 Yielded 15 and 16a. 16a: bp 68-75° (5 mm); ir 2830 (methoxy), 1700, 1250 cm^{-1} (ester); NMR (CCl_4) τ 4.93 (broad s, 1, O-CH-N), 6.32 (s, 3, CO_2CH_3), 6.78 (s, 3, methoxy), 6.79-7.18 (m, 2, $-CH_2-N$), 8.15-8.80 (m, 4), 9.17 (t, 3, $-CH_3$). Anal. Calcd for $C_9H_9NO_3$: C, 57.11; H, 10.12; N, 7.40. Found: C, 56.99; H, 10.27; N, 7.30.

Electrolysis of 17. The product was **17a:** bp 90-96° (3 mm); ir 2840 (methoxy), 1700, 1200 cm^{-1} (ester); NMR (CCl_4) τ 4.90 (broad s, 1, N-CH-O), 6.38 (s, 3, CO_2CH_3), 6.90 (s, 3, methoxy), 6.75-7.07 (t, 2, $-CH_2-N$), 8.50 (m, 8), 9.00 (t, 3, $-CH_3$). Anal. Calcd for $C_{11}H_{23}NO_3$: C, 60.80; H, 10.67; N, 6.45. Found: C, 60.55; H, 10.55; N, 6.55.

Electrolysis of 10. The products consisted of **10a** and **10b. 10a:** bp 64° (4 mm); ir 2840 (methoxy), 1700, 1260 cm^{-1} (ester); NMR (CCl_4) τ 4.78 (broad s, 1, O-CH-N), 6.30 (s, 3, CO_2CH_3), 6.32-6.85 (m, 2, $-CH_2-N$), 6.80 (s, 3, methoxy), 8.18-8.50 (m, 6). Anal. Calcd for $C_9H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.49; H, 8.90; N, 8.25.

10b: bp 58° (4 mm); ir 3010 (olefin), 2840 (methoxy), 1700 (ester), 1650 cm^{-1} (olefin); NMR (CCl_4) τ 3.30 (broad s, 1, C=CHN), 5.26 (broad s, 1, HC=CN), 6.30 (s, 3, CO_2CH_3), 6.33-6.60 (m, 2, $-CH_2-N$), 7.90-8.45 (m, 4). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.28; H, 7.84; N, 9.65.

Electrolysis of 18 Gave 18a. 18a: bp 60° (4 mm); ir 2840 (methoxy), 1700, 1245 cm^{-1} (ester); NMR (CCl_4) τ 5.85 (broad s, 1, OCH-N), 6.30 (s, 3, CO_2CH_3), 6.50-6.75 (m, 2, $-CH_2-N$), 6.67 (s, 3, methoxy), 8.10 (m, 4). Anal. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80. Found: C, 52.84; H, 8.42; N, 8.97.

Electrolysis of 19 yielded methyl carbamate. Methyl carbamate was identified by comparison of its ir and the retention time of gas chromatograph (column, silicon DC550, PEG20M) with those of authentic sample.[21]

Electrolysis of 20 yielded dealkylated product **19** in a yield of 15%.

Electrolysis of 21 gave methyl carbamate and cyclohexanone.

Electrolysis of 22. The product was **22a:** bp 85° (3 mm); ir 2835 (methoxy), 1700, 1260 cm^{-1} (ester); NMR (CCl_4) τ 5.38 (s, 2, $N-CH_2-O$), 6.36 (s, 3, CO_2CH_3), 6.80 (s, 3, methoxy), 6.72-6.84 (t, 2, $-CH_2-N$), 8.38-8.86 (m, 4), 9.05 (t, 3, $-CH_3$). Anal. Calcd for $C_8H_{17}NO_3$: C, 54.83; H, 9.78; N, 7.99. Found: C, 54.58; H, 9.90; N, 8.03.

Electrolysis of 23 Yielded 23a. 23a: bp 83° (3 mm); ir 2840 (methoxy), 1700, 1300 cm^{-1} (ester); NMR (CCl_4) τ 5.24 (s, 2, $N-CH_2-O$), 6.40 (s, 3, CO_2CH_3), 6.40 (m, 1, -CH-N), 6.90 (s, 3, methoxy), 8.00-8.98 (m, 8). Anal. Calcd for $C_9H_{18}NO_3$: C, 59.67; H, 9.52; N, 6.96. Found: C, 59.63; H, 9.81; N, 7.06.

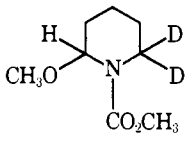
Electrolysis of 24. The products consisted of **24a** and **24a'. 24a:** bp 110° (5 mm); ir 3010 (aromatic), 2835 (methoxy), 1695, 1250 (ester), 765, 705 cm^{-1} (aromatic); NMR (CCl_4) τ 2.89 (s, 5, aromatic), 3.68 (s, 1, C_6H_5CH), 6.28 (s, 3, CO_2CH_3), 6.60 (s, 3, methoxy), 7.50 (s, 3, $N-CH_3$). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.11; H, 7.27; N, 6.70.

24a': bp 110° (5 mm); ir 3010 (aromatic), 2835 (methoxy), 1700, 1250 (ester), 765, 705 cm^{-1} (aromatic); NMR (CCl_4) τ 2.89 (s, 5, aromatic), 5.40 (s, 2, $O-CH_2-N$), 5.55 (s, 2, $C_6H_5-CH_2N$), 6.30 (s, 3, CO_2CH_3), 6.79 (s, 3 methoxy). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.90; H, 7.21; N, 6.73.

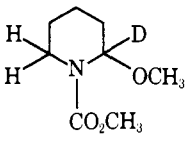
Electrolysis of 25 in methanol did not give any product, and the starting material was recovered with 98% yield.

Measurements of Isotope Effects. Electrochemical Oxidation of 9. A methanolic solution (19.25 ml) of **9** (20.02 mmol) containing

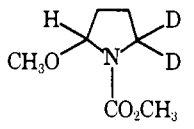
Et_4NOTs (2.00 mmol) was anodically oxidized for 2.4 hr. After the reaction, work-up gave a methoxylated product whose retention time of VPC and the pattern of the NMR spectrum were identical with those of *N*-carbomethoxy-α-methoxypiperidine, indicating that the methoxylated product consisted of **9a** and **9b**. The ratio of **9a** and **9b** was obtained from the intensity of NMR peaks



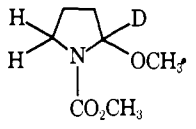
9a



9b



12a

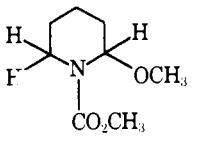


12b

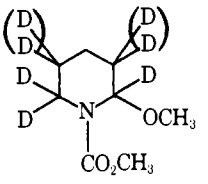
of α proton and methoxy proton.

Electrochemical Oxidation of 12. Anodic oxidation of **12** (13.42 mmol) in methanol (8.61 ml) containing Et_4NOTs (1.34 mmol) was carried out for 1.5 hr. The ratio of products **12a** and **12b** was calculated by the NMR method as described above.

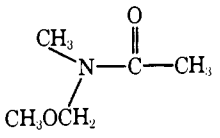
Competitive Reaction of 10 and 11. A mixture of **10** (10.11 mmol) and **11** (10.11 mmol) was electrolyzed in 12.8 ml of methanol containing Et_4NOTs (2.00 mmol). The reaction mixture was worked up at the stage where the conversion of the reaction was reached to 20%. The value of the intermolecular isotope effect was



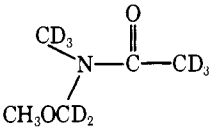
10a



11a



13a



14a

obtained by calculating the ratio of **10a** and **11a** by the NMR method.

Competitive Reaction of 13 and 14. A mixture of **13** (20.21 mmol) and **14** (20.21 mmol) was anodically oxidized in methanol (25.63 ml) containing Et_4NOTs (4.04 mmol). The ratio of products **13a** and **14a** was calculated in a similar method as described above. The conversion of the reaction was 20%.

Preparation of 8. Electrolysis of methyl *N*-methyl-2-hydroxyethylcarbamate prepared from *N*-methyl-2-ethanolamine in methanol gave **8** in a yield of 60%. **8:** bp 75° (30 mm); ir 2855 (methoxy), 1760 cm^{-1} (ester); NMR (CCl_4) τ 5.27 (s, 2, $N-CH_2-O$), 5.98 (t, 2, $O-CH_2-$), 6.16 (s, 3, CO_2CH_3), 6.73 (t, 2, $N-CH_2-$).

Reaction of 10a with *p*-Toluenesulfonic Acid. A mixture of 0.025 *M* of **10a** and 300 mg of *p*-toluenesulfonic acid in 30 ml of benzene was refluxed for 12 hr and after benzene was distilled off, enamine type product **10b** was distilled, the yield being 95%.

Oxidation Potential. The data were obtained at room temperature on a Yanako P-8DP (Yanagimoto Co. Ltd). Oxidation was carried out in dry acetonitrile at a rotating platium electrode with 0.1 *M* Et_4NOTs using an aqueous saturated calomel reference electrode. The concentration of substrate was 2×10^{-4} *M* and an H-type electrolysis cell was used.

References and Notes

(1) Part XIX: T. Shono, A. Ikeda, J. Hayashi, and S. Hakozaki, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966).
(3) (a) K. K. Barnes and C. K. Mann, *J. Org. Chem.*, **32**, 1474 (1967); (b) P. J. Smith and C. K. Mann, *ibid.*, **34**, 1821 (1969).
(4) N. L. Weinberg and T. B. Reddy, *J. Am. Chem. Soc.*, **90**, 91 (1968).
(5) J. E. Barry, M. Finkelstein, E. A. Mayeda, and S. D. Ross, *J. Org. Chem.*, **39**, 2695 (1974).
(6) L. C. Portis, V. V. Bhat, and C. K. Mann, *J. Org. Chem.*, **35**, 2175 (1970).
(7) The deuterium contents of starting materials and products were invariant under the reaction condition.
(8) The inter- and intramolecular isotope effects were almost identical (3.2)[10] in the homolytic α substitution of some saturated ethers by the Kharasch–Sosnovsky reaction where the active species is *tert*-butoxy radical.[11]
(9) The isotope effect measured in the homolytic α-hydrogen abstraction from an alkylamine by chlorine dioxide is 5.0.[12]
(10) T. Shono and Y. Matsumura, to be published.
(11) (a) G. Sosnovsky and S. Lawesson, *Angew. Chem.*, **76**, 218 (1964); (b) S. Lawesson and C. Berglurd, *Ark. Kemi*, **17**, 465 (1961).
(12) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *J. Am. Chem. Soc.*, **89**, 1163 (1967).
(13) The intramolecular isotope effect of the anodic allylic substitution of cyclohexene based on the similar energetic difference is 1.6[14] which is comparable to those shown in Table III.
(14) T. Shono and A. Ikeda, *J. Am. Chem. Soc.*, **94**, 7892 (1972).
(15) A potential difference of 1.0 V is equivalent to an energy difference of 23 kcal.[16]
(16) L. Eberson and K. Nyberg, *Acc. Chem. Res.*, **6**, 106 (1973).
(17) W. M. Kraft and R. M. Herbert, *J. Org. Chem.*, **10**, 483 (1945).
(18) R. B. Moffett, "Organic Synthesis", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 355.
(19) C. S. Marvel and J. C. Eck, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1961, p 371.
(20) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).
(21) L. Birckenbach and H. Kolb, *Chem. Ber.*, **68**, 901 (1935).