Electroorganic Chemistry. XIX.[1] Anodic Oxidation of Nonconjugated Dienes

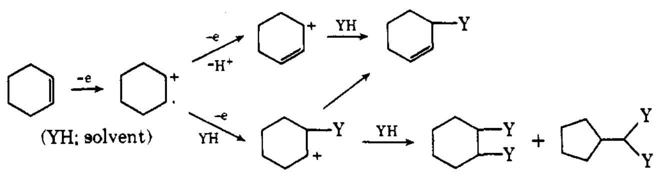
T. Shono,* A. Ikeda, J. Hayashi, and S. Hakozaki

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received January 29, 1975*

Abstract: Anodic oxidation of nonconjugated dienes in methanol or acetic acid was investigated. Norbornadiene or bicyclo[2.2.2]octadiene gave transannularly interacted products and 1,5-cyclooctadiene showed little transannular interaction, whereas limonene or 4-vinylcyclohexene did not show such an interaction but yielded the products where the intra-ring double bond was exclusively oxidized. The oxidation potential of norbornadiene was much lower than that of norbornene, while limonene showed the same oxidation potential as that of 1-methylcyclohexene. The oxidation potentials of 2-substituted norbornenes, 2-substituted bicyclo[2.2.2]octadienes, and 4-substituted [2.2]paracyclophanes were measured, and good linear relationships were observed between the oxidation potentials and $\sigma_p{}^+$ of the substituent.

It was found in our continuing study on the organic electrode reaction that in a certain solvent the anodic oxidation of an aliphatic olefin bearing at least one allylic hydrogen resulted in a novel allylic substitution reaction in which the solvent molecule behaved as a nucleophile.[2,3] A typical example and its reaction pathway are shown in Scheme I,

Scheme I



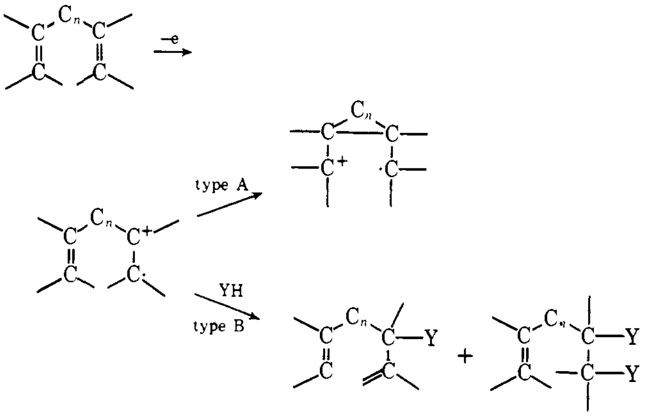
where the initial reactive species was a cation radical generated by anodic one-electron elimination from the olefinic π-electron system.

In the present study, the chemical behavior of the cation radical generated from nonconjugated diene systems was investigated because of our interest in the interaction between the olefinic bonds, and the oxidation potentials of 2-substituted norbornadiene, bicyclo[2.2.2]octa-2,5-diene, and 4-substituted [2.2]paracyclophane were measured to clarify the contribution of such an interaction to the anodic electron transfer process.

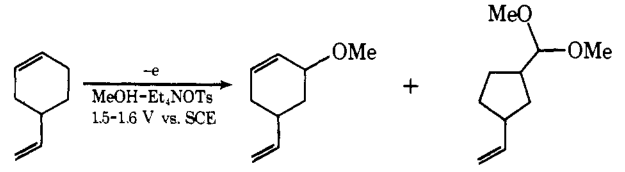
Results and Discussion

Anodic Oxidation of Nonconjugated Dienes. As shown in Scheme II, the possible reaction pathway of the anodic oxidation of nonconjugated diene could be classified into the following two categories. Type A: one electron is removed from one double bond to yield a cation radical followed by the transannular reaction of the cation radical with another double bond to form a new carbon–carbon bond. Type B: allylic substitution or oxidative addition at one double bond occurs without the intramolecular interaction of both double bonds.

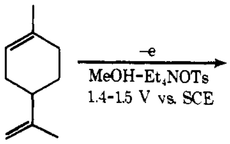
Scheme II

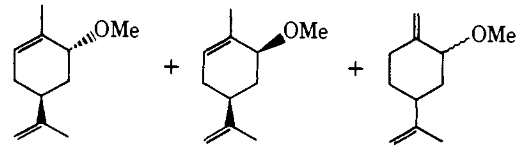


The anodic oxidation of 4-vinylcyclohexene or limonene carried out in methanol containing tetraethylammonium p-toluenesulfonate as a supporting electrolyte gave the products classified to type B. The current efficiency shown was determined at the stage where 2 Faradays/mol of electricity was passed. The products showed interesting selectivity in which the intra-ring double bond was exclusively oxidized suggesting that the selectivity was brought about by the difference of the oxidation potential between two double bonds.

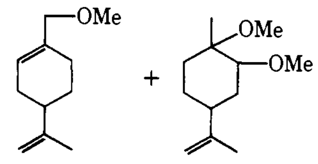


1 (32.2%) **2** (21.3%)





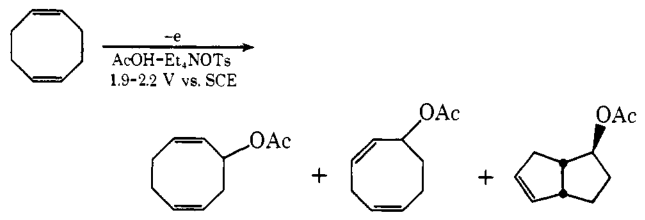
3 (20.5%) **4** (6.5%) **5** (15.7%)



6 (2.5%) **7** (8.9%)

The anodic oxidation of 1,5-cyclooctadiene, which shows a great tendency to yield a transannularly interacted product in the cationic reactions,[4] gave the product **10**, classified as type A in a very low yield.

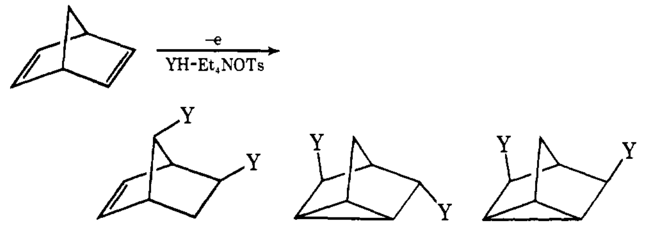
The low degree of transannular interaction might be ex-



8 (8.9%) 9 (2.1%) 10 (1.0%)

plainable by the large steric hindrance attributable to the electrode.

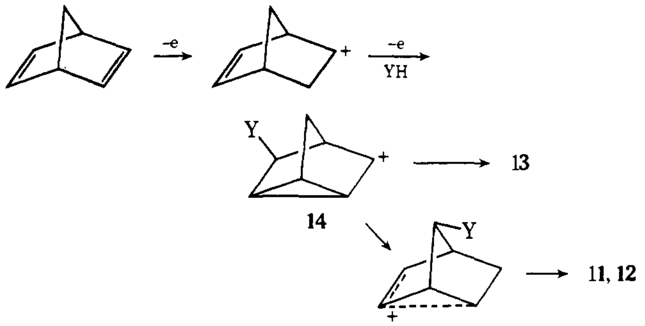
On the other hand, the electrooxidation of norbornadiene, in which two double bonds are suitably arranged for the transannular interaction, yielded the products classified as type A.



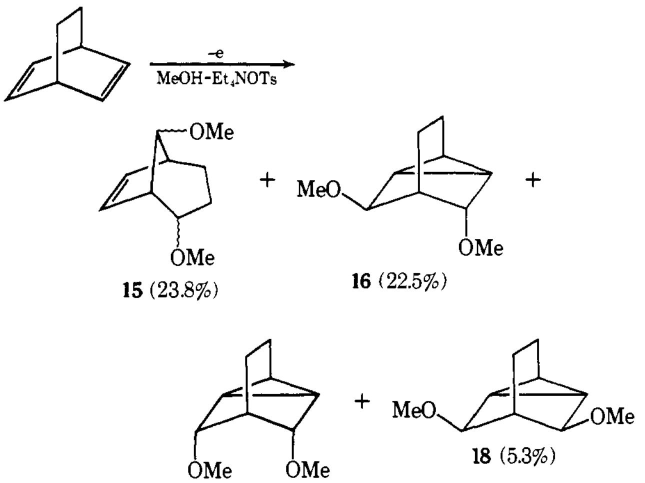
	11a, b	12a, b	13a, b
a, Y = OAc	6.2%	14.1%	15.4%
b, Y = OMe	8.8%	16.5%	18.4%

The formation of these products could be elucidated by the mechanism depicted in Scheme III.

Scheme III



The formation of the intermediate **14** (Y = OAc) has been suggested in the acetolysis of a ditosylate of norbornene-5,6-diol which yielded the same products indicated in Scheme III.[5] In contrast to norbornadiene, bicyclo[2.2.2]octadiene-2,5 does not always give the transannularly interacted product in the usual solution reaction,[6,7] whereas in the anodic oxidation, the octadiene showed exclusive transannular interaction.



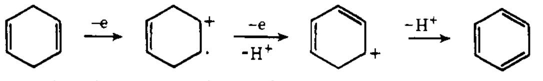
15 (23.8%) **16** (22.5%) **17** (9.1%) **18** (5.3%)

Table I. The Oxidation Potentials of Some Dienes and Olefins (V vs. SCE)[a]

1-Methylcyclohexene	1.70	Norbornadiene	1.54
Limonene	1.67	Bicyclo[2.2.2]-octadiene	1.82
Cyclooctene	2.01	Cyclohexene	2.14
1,5-Cyclooctadiene	2.07		
Norbornene	2.02	1,4-Cyclohexadiene	1.74

[a] Studied with a three-electrode polarograph using a rotating platinum electrode in acetonitrile containing 0.1 *M* lithium perchlorate.

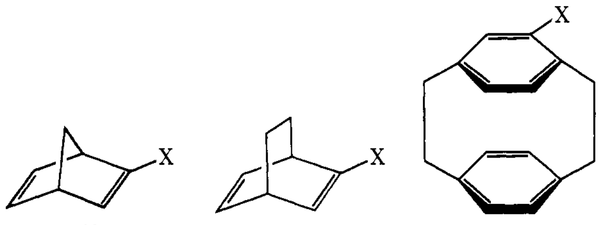
The electrooxidation of 1,4-cyclohexadiene in acetic acid or methanol gave only one volatile product, benzene, in the current efficiency of 55 or 71%, respectively. The formation of benzene could be rationalized by the following scheme.



The oxidation potentials of some nonconjugated dienes and corresponding olefins are summarized in Table I. The oxidation potentials of 1,5-cyclooctadiene and limonene which give little or no transannularity interacted product are substantially the same as those of corresponding monoolefins, cyclooctene and 1-methylcyclohexene, whereas norbornadiene and bicyclo[2.2.2]octadiene, which give the products of type A, show much lower oxidation potential than that of norbornene. This result would be explainable in terms of the stabilization of the cation radical by the transannular interaction with another double bond.

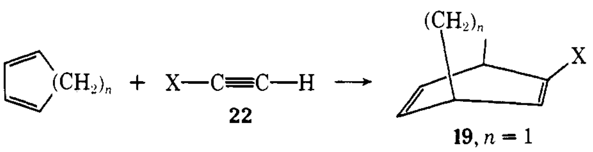
The Intramolecular Interaction between Two Unsaturated Systems in the Anodic Electron Transfer Process. As mentioned above, some dienes where two double bonds are suitably arranged for the mutual interaction yielded a considerable amount of products which suggests the existence of the transannular interaction. However, the contribution of the interaction between two unsaturated systems to the anodic electron transfer process could not be established only on the basis of the structure of the products.

To clarify the participation of such an interaction, the oxidation potentials of 2-substituted norbornadiene (**19**), bicyclo[2.2.2]octa-2,5-dienes (**20**), and 4-substituted [2.2]paracyclophane (**21**) were measured.



19 **20** **21**

The substituted dienes **19** and **20** were prepared by the Diels–Alder reaction of substituted acetylenes **22** with corresponding dienes.



19, $n = 1$
20, $n = 2$

The oxidation potentials of these compounds are shown in Table II.

Table II. The Oxidation Potentials of **19**, **20**, and **21**

Substituent (X)		Oxidation potential (V vs. SCE)		
		19	20	**21**
a	H	1.54	1.82	1.47
b	CO_2CH_3			1.61
c	$CO_2CH_2CH_3$	1.85	2.11	
d	$COCH_3$	1.85	2.07	1.57
e	CN	1.99	2.22	1.65
f	NO_2			1.72

Figure 1 exhibits the plots of oxidation potentials vs. $\sigma_p{}^+$. Although the coefficient $\sigma_p{}^+$ is not necessarily ideally applicable to the cation radical system, the best linear relationship was given by using $\sigma_p{}^+$.

The result shown in Figure 1 strongly suggests the existence of nonbonding interaction in the process of the anodic electron transfer from the compound **19, 20,** or **21,** where the electron is removed from the unsaturated system not substituted with the electron withdrawing group.

This result would afford the first convincing evidence to support the contribution of such an interaction to the anodic electron transfer from nonconjugated dienes or related systems.[8]

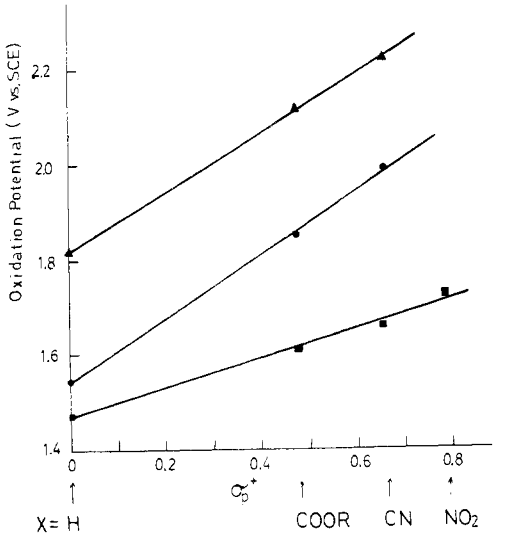


Figure 1. Plots of the oxidation potentials of **19** (●), **20** (▲), and **21** (■) vs. $\sigma_p{}^+$.

Experimental Section

Electrooxidation of dienes was carried out in a similar manner described in the previous report.[2] The products were isolated roughly by distillation under reduced pressure and purified with the preparative gas chromatograph.

Anodic oxidation of 4-vinylcyclohexene in methanol gave **1** and **2. 1:** bp 75-80° (20 mm); ir 3100, 3045 (H-C=), 2830 (OCH_3), 1640 (C=C), 1100 (-O-), 990, 910 cm^{-1} (H-C=); NMR (CCl_4) τ 3.9-4.5 (m, 3 H, =CH), 4.7-5.3 (m, 2 H, CH_2C=), 6.3-6.6 (m, 1 H, CH-OMe), 6.73 (s, 3 H, OCH_3), 7.5-9.0 (m, 5 H, aliphatic). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.48; H, 10.18.

2: bp 92-95° (20 mm); ir 3100 (H-C=), 2850 (OMe), 1640 (C=C), 1220-1160 (-O-), 990, 905 cm^{-1} (H-C=); NMR (CCl_4) τ 3.9-4.5 (m, 1 H, =CH), 4.8-5.3 (m, 2 H, H_2C=), 6.00 (d, J = 7.5 Hz, 1 H, CHOMe), 6.78 (s, 6 H, OCH_3), 7.3-9.2 (m, 8 H, aliphatic). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.40; H, 10.48.

Limonene yielded **3** (cis), **4** (trans), **5, 6,** and **7.** NMR and ir spectra of **3, 4, 5,** or **6** are identical with those of the products of the electrooxidation of pinene in methanol.[2]

Electrooxidation of 1,5-cyclooctadiene in acetic acid gave **8, 9,** and **10.** The identification of **8** or **9** was accomplished by the comparison of its spectra with those of authentic samples.[7] The structure of **10** was confirmed by the following method. Product **10** was hydrogenated on palladium-charcoal (10%). The ir spectrum of the hydrogenated product was identical with that of the authentic *endo*-acetoxybicyclo[3.3.0]octane.[4]

Anodic Oxidation of Norbornene in Acetic Acid. Products were **11a, 12a,** and **13a. 12a:** ir 3080 (cyclopropane), 1730 (C=O), 1240 (-O-), 820 cm^{-1} (characteristic absorption of nortricyclenes); NMR (CCl_4) τ 4.86-5.03 (m, 1 H, CH-OAc), 5.25-5.45 (m, 1 H, CH-OAc), 7.98 (s, 3 H, $OCOCH_3$), 8.02 (s, 3 H, $OCOCH_3$), 7.7-8.0 (m, 1 H, bridgehead proton). Anal. Calcd for $C_{11}H_{14}O_2$: C, 62.84; H, 6.71. Found: C, 62.64; H, 6.92.

13a: ir 3080 (cyclopropane), 1730 (C=O), 1235, 1030 (-O-), 815 cm^{-1} (nortricyclene); NMR (CCl_4) τ 4.66 (m, 2 H, CH-OAc), 3.63-3.80 (m, 1 H, bridgehead), 8.03 (s, 6 H, $OCOCH_3$), 8.05-8.23 (m, 2 H, bridge), 8.4-8.7 (m, 3 H, cyclopropane). Anal. Calcd for $C_{11}H_{14}O_2$: C, 62.84; H, 6.71, Found: C, 62.97; H, 6.85. NMR spectrum of **11a** was identical with authentic spectrum.[10]

In methanol, norbornadiene yielded **11b, 12b,** and **13b. 11b** was identified on the basis of the comparison of the spectral data with those of the authentic sample synthesized by methoxylation of *exo*-2-*syn*-7-norbornenediol.[8] **12b:** ir 3065 (cyclopropane), 2825 (OCH_3), 1100 (-O-), 800 cm^{-1} (nortricyclene); NMR (CCl_4) τ 6.03-6.20 (m, 1 H, HC-OMe), 6.50-5.63 (m, 1 H, CHOMe), 6.75 (s, 6 H, OCH_3), 7.95-8.40 (m, 3 H, bridge and bridgehead), 8.55-8.80 (m, 3 H, cyclopropane). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.92; H, 9.41. **13b:** ir 3070 (cyclopropane), 2830 (OMe), 1090 (-O-), 800 cm^{-1} (nortricyclene); NMR (CCl_4) τ 6.50-6.95 (m, 2 H, CHOMe), 6.81 (s, 6 H, OCH_3), 7.80-8.00 (m, 2 H, bridge), 8.69 (broad s, 3 H, cyclopropane). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.91; H, 9.33.

Bicyclo[2.2.2]octadiene-1,5, prepared according to the reported method,[11] was electrolyzed in methanol to give four products **15, 16, 17,** and **18. 17** was thought to be 2,8-dimethoxybicyclo[3.2.1]octene-6. **15:** ir (CCl_4) 3050, (H-C=), 2840 (OCH_3), 1105 cm^{-1} (-O-); NMR (CCl_4) τ 3.85-4.70 (m, 2 H, CH=), 6.47 (broads, 1 H, CHOMe), 6.57 (broad t, J = 3 Hz, 1 H, CH-OMe), 6.67 (s, 3 H, OCH_3), 6.76 (s, 3 H, OCH_3), 7.3-7.8 (m, 1 H, =C-CH), 7.8-9.3 (m, 4 H, aliphatic); mass spectrum *m/e* (relative intensity) 136 (P^+ − 32, 11), 108 (100), 104 (P^+ − 64, 21), 84 (39).

Structural assignment of **16, 17,** and **18** was accomplished by means of their NMR and ir spectra. The absorption in their ir spectra at 3060 cm^{-1} and the absence of the olefinic proton peak in their NMR suggested the presence of a cyclopropane ring. From an analogy with the case of the anodic methoxylation of norbornadiene, these compounds were inferred to be isomers of 3,5-dimethoxytricyclo[2.2.2.$0^{2,6}$]octane. The NMR spectra were in accord with this structure. On the basis of the signals assigned to methoxy protons, it could be concluded that **17** or **18** possesses two equivalent methoxy groups and **16** is an unsymmetrical exo-endo structure. NMR of **16** shows two separated peaks assigned to methines bearing the methoxy group; one is a broad singlet at τ 6.46 and another is a multiplet at 5.88-6.12, which would be respectively assigned to exo (H(x)) and endo (H(n)) protons on the basis of the coupling constant estimated from the dihedral angle and the reported NMR data for analogous compounds.[12] Since the peak of the equivalent methines in **17** or **18** is a broad singlet or multiplet, **17** or **18** was assigned to endo-endo or exo-exo structure respectively.

16: ir (CCl_4) 3060 (cyclopropane), 2840 (OCH_3), 1110 cm^{-1} (-O-); NMR (CCl_4) τ 5.88-6.12 (m, 1 H, endo CH-OMe), 6.46 (broad s, 1 H, exo CH-OMe), 6.67 (s, 3 H, OCH_3), 6.74 (s, 3 H, OCH_3), 7.9-9.2 (m, 8 H, aliphatic); mass spectrum *m/e* (relative intensity) 136 (P^+ − 32, 0.8), 104 (P^+ − 64, 1), 97 (100), 75 (41).

17: ir (CCl_4) 3060 (cyclopropane), 2840 (OMe), 1120 cm^{-1} (-O-); NMR (CCl_4) τ 6.59 (broad s, 2 H, CH-OMe), 6.75 (s, 6 H, OCH_3), 7.8-8.0 (m, 1 H, CH-C-OMe), 8.1-9.3 (m, 7 H, aliphatic); mass spectrum *m/e* (relative intensity) 168 (P^+, 0.5), 149 (4), 136 (P^+ − 32, 39), 104 (P^+ − 64, 18), 88 (48), 84 (100).

18: ir (CCl_4) 3050 (cyclopropane), 2840 (OCH_3), 1100 cm^{-1} (-O-); NMR (CCl_4) τ 6.2-6.4 (m, 2 H, CH-OMe), 6.67 (s, 6 H, OCH_3), 7.8-9.4 (m, 8 H, aliphatic).

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).

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(8) The interaction between nonconjugated double bonds in the cathodic reduction has been studied in some systems.[9]

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

T. Shono,* H. Hamaguchi, and Y. Matsumura

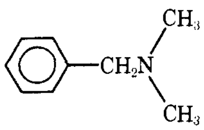
Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

Received January 29, 1975

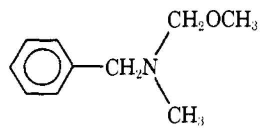
Abstract: The anodic oxidation of methyl *N,N*-dialkylcarbamate (**4**) in methanol yielded three types of products, that is, α-methoxylated compound (**5**), enamine-type product (**6**) and dealkylated carbamate (**7**). Inter- and intramolecular isotope effects were measured to be 1.5–1.6 and 1.8–1.9, 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 *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]



1



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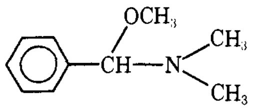
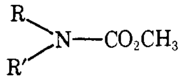


3

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

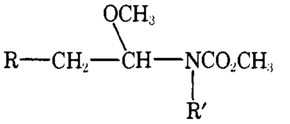


4

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

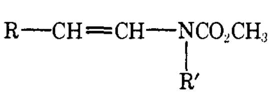
Results

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 carbamate (**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%.



$R-CH_2-CH(OCH_3)-N(R')CO_2CH_3$

5



$R-CH=CH-N(R')CO_2CH_3$

6

$R'-NHCO_2CH_3$

7