one. The K-region oxide (7) is not the major activated form of the potent mutagenic parent compound (3). Interestingly the N-oxide (12) was weakly mutagenic to TA 100 without S-9 Mix. Contrary to those K-region oxides of dibenzacridines, the K-region oxide (**8**) of **4** was quite strongly active to TA 98 and TA 100 without S-9 Mix. Therefore **8** seems to be one of the important ultimate mutagens of **4**. The dose response curves of **8** and benzo[*a*]-pyrene-4,5-oxide (**14**) without S-9 Mix were shown in Fig. 1 and 2. The result suggests that **8** is more stronger than **14** to TA 98 in the present assay system. A further metabolism by S-9 Mix is detoxificative as the case of **14**. We are trying to synthesize a potent arene oxide of **3**, and to identify the metabolites of **4**.

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Electrolytic Intramolecular Cyclization of N-Alkylcarboxanilides to Benzoxazolium

Anodic oxidation of N-alkylcarboxanilides in methanol at controlled potentials resulted in the formation of N-alkylbenzoxazolium perchlorate *via* nucleophilic attack of the carbonyl oxygen to the phenyl ring.

Keywords——N-alkylcarboxanilides; intramolecular cyclization; benzoxazolium; anodic oxidation; controlled potential electrolysis; cyclic voltammetry;

Oxidations of alkyl- and aryl-thioanilides have long been known as a method to prepare benzothiazoles.[1] However, oxidations of carboxamides usually caused C-C or C-N bond fisssion, and/or substitution reactions.[2] There seems to be no publication on the oxidation of carboxanilides to form benzoxazoles,[3] though a few papers have reported intramolecular oxidative cyclization with carboxamide oxygen: the formation of benzocoumarines as trace or minor products *via* amidyl radicals in the persulphate oxidation of *o*-phenylbenzamides,[4] and the electrochemical oxidation of phloretylglycine to give a dienone lactone.[5]

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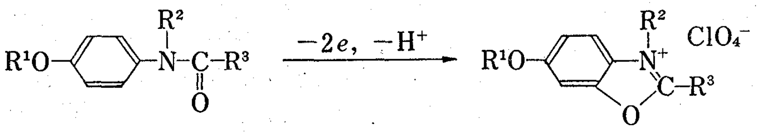

I	R^1	R^2	R^3
a:	Me	Me	Me
b:	Me	Me	Ph
c:	Me	Pr^i	Me

II

Ph=phenyl

Chart 1

We report here a novel anodic cyclization of N-alkylcarboxanilides (I) to produce benzoxazolium (II) *via* nucleophilic attack of the carbonyl oxygen to the phenyl ring. Anilide (Ia) was subjected to electrolysis in methanol containing 0.1 M sodium perchlorate at 1.3V *vs* SCE at a glassy carbon plate electrode in a divided cell at 0°. About 2 F mol^{-1} of electricity were consumed. White needles which deposited during the electrolysis were filtered off and recrystallized from methanol, and the product was identified as 2,3-dimethyl-6-methoxybenzoxazolium perchlorate (IIa) by ultraviolet, infrared, and nuclear magnetic resonance spectra and by elemental analysis. Compounds (IIb) and (IIc) were obtained similarly.

The results of cyclic voltammetry and controlled potential electrolysis of (I) are summarized in Table I. Electrolysis of (I) in acetonitrile containing 1% methanol gave similar results.

Table I. Results of Cyclic Voltammetry and Controlled Potential Electrolysis of (I) in Methanol[a)]

Substrate	E_p/V *vs* SCE[b)]	*n*-Value[c)]	Yield/%
Ia	1.30	2.1	70
Ib	1.27	2.2	73
Ic	1.47	7[d)]	10[d)]

a) 0.1 M $NaClO_4$.
b) Glassy carbon electrode (3 mm ϕ); sweep rate, 100 mV s^{-1}.
c) Electrolyses were carried out at the corresponding peak potential.
d) The high *n*-value and the low yield may be ascribed either to the decomposition of IIc or to the ring methoxylation to form compounds which are further oxidized at the applied potential.

The voltammetric behavior of (I) in the present solvent system was essentially the same as that in acetonitrile with and without added water,[6)] indicating that the initial step of the oxidation involves a two-electron transfer from the substrate to form a dication. However, in acetonitrile without methanol entirely different products were formed,[6)] although electrochemical oxidation of thiobenzanilide in acetonitrile was reported to give 2-phenylbenzothiazole.[7)] It is interesting to note that no cyclization product is obtained on electrolysis of benzanisidide, which has a hydrogen atom on the anilide nitrogen, both in acetonitrile[8)] and in methanol. These observations suggest that the mechanism of electrochemical cyclization of (I) is different from that of thioanilides. Detailed studies on the scope and the mechanism of the reaction are in progress.

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