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Electrochemical Oxidation of Methanolic Solution of Sodium Cyanide. A Facile Formation of Dimethyl Oxaldiimidate

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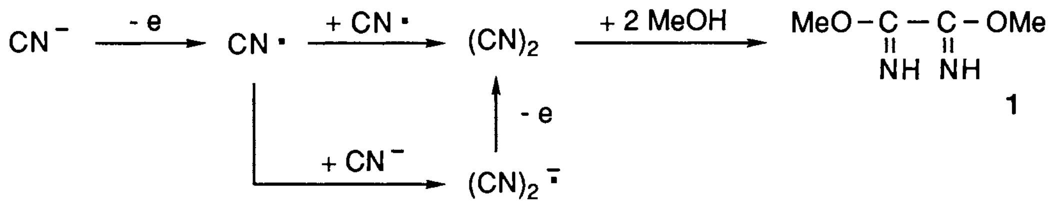
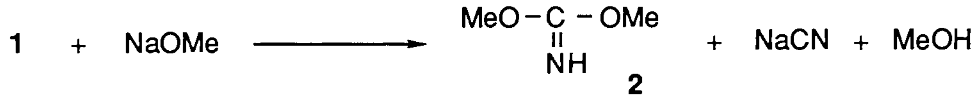
Dimethyl oxaldiimidate could be obtained in good yield by the electrolytic oxidation of methanolic solution of sodium cyanide in a divided cell using a carbon anode. Analogous electrolysis in an undivided cell gave dimethyl imidocarbonate as the main product.

The electrochemical oxidation of cyanide ion has widely been investigated by using a platinum anode,[1a-d] and it has been postulated that cyanide ion is electrooxidized to give cyanogen initially, while the identification of the intermediate has been unsuccessful, because it imediately undergoes further reaction under such conditions. In example of the anodic oxidation of cyanide ion in aqueous solution, many kinds of products are formed, such as the carbonate, nitrogen, ammonia, and urea along with brown residue, resulting from the decomposition of cyanogen and the cyanate.[2a,b]

In our study of electrolytic oxidation of organic compounds in NaCN-MeOH,[3] we observed the formation of a small amount of dimethyl oxaldiimidate (**1**), presumably derived from the intermediary cyanogen by the methanolysis. Thus, we attempted the electrolytic oxidation of NaCN-MeOH in the absence of organic substrate and found that cyanide ion quite readily discharges at a carbon anode, affording oxaldiimidate **1** in good yield. We describe in this paper the electrooxidative preparation of **1** which is valuable intermediate in a variety of heterocyclic syntheses.[4]

The preparative electrolysis was carried out in a divided cell equipped with four carbon rods (5-mm dia × 100 mm) as the anode. A typical procedure is as follows. A solution of





sodium cyanide (5.0 g, 0.10 mol) in methanol (100 ml) was electrooxidized under a condition of constant current of 1 A and ice cooled temperature. After 1.2 F/mol of electricity had passed (the terminal voltage gradually increased and no more product was formed), the solvent was evaporated in vacuo at room temperature, and the residue was treated with brine. The organic layer was extracted with ether (20 ml × 4), dried (K_2CO_3), and distilled in vacuo. Almost pure **1** was obtained as colorless oil in a yield of 70%, which was solidified on standing.5)

The analogous electrolysis using a glass filter (No. 5) or in an undivided celll gave dimethyl imidocarbonate (**2**) as the main product in a yield of 48%.6) It is highly probable that the produced **1** underwent alkaline induced decomposition to **2** by sodium methoxide generated at the cathode. In fact, **1** was readily converted into **2** by treatment with NaOMe-MeOH at room temperature. Accordingly, in order to obtain satisfactory yield of **1**, it was necessary to prevent the leakage of the catholyte to the anolyte. For this purpose, a porous porcelain cup was used as the cell membrane and small portions of acetic acid were added at hourly intervals during the electrolysis to keep the anolyte weak alkaline.

In the present reaction, it is reasonable to assume that cyanide ion is oxidized to cyanogen as has already been reported,1b,d) which imediately reacts with methanol to give diimidate **1**, since the addition of simple alcohols to cyanogen readily takes place under the alkaline conditions.7) Although the formation of **1** was successfully performed by using the carbon anode, the use of platinum anode caused the formation of tarry material from which no product could be isolated. The difference between results obtained on the cabon anode and platinum may primarily be attributable to the readiness of the oxidation of cyanide ion at each electrode. Figure 1 shows the result of voltammetric experiment. As can be seen

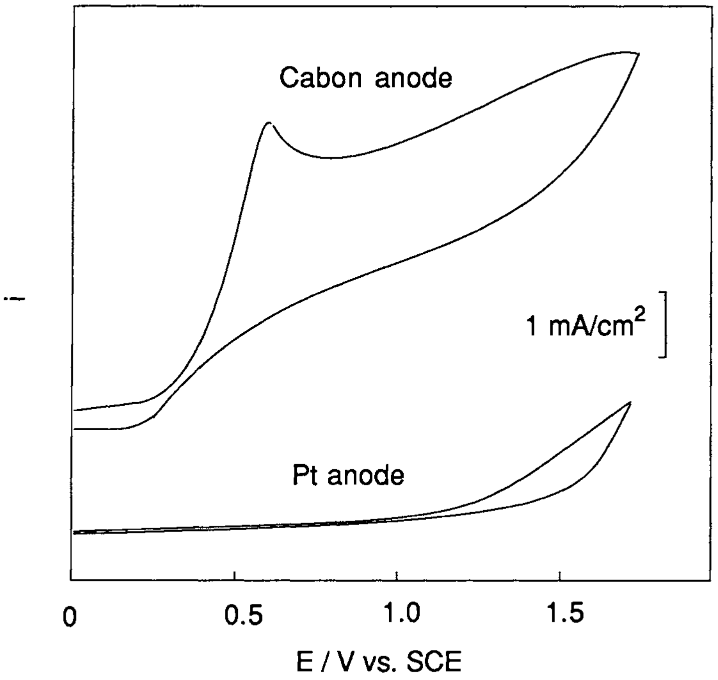


Fig. 1. Cyclic voltammograms of NaCN/MeOH at carbon and platinum anode. Concentration: 50 mM. Scan rate: 0.1 V/s.

from the result, the methanolic solution of sodium cyanide was oxidized sufficiently at a carbon anode even at the potential of 0.5 V vs. SCE, whereas at a platinum anode it was not discharged unless the anode potential exceeded 1.2 V. The high oxidation potential owing to the strong adsorption of cyanide ion on the platinum in methanol would result in further electrode reaction of cyanogen to lead paracyan, etc.[1c)]

Usually, oxaldiimidates are prepared by the reaction of cyanogen with aqueous alcohol in the presence of pottasium cyanide,[7a-c)] however, this method is encountered a laborious task associated with handling the highly poisonous gas. The present method seems to be preferable in that diimidate **1** can be prepared directly from sodium cyanide without the use of oxidizing reagent by simple operation.

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5) The product **1** was somewhat unstable, turning yellow and finaly brown at room temperature, but easily purified by distillation or by recrystallization from hexane. It is recomended to store in a refrigerator, protecting from light. The identification of the product was conducted by comparison with an authentic sample prepared by Nef's method(Ref. 7a). **1**: Mp 32-34 °C, Bp 44 °C (15 Torr); IR (neat) ν 3250, 1610, 1430, 1270, 1060, 850 $\mathrm{cm^{-1}}$; $^1\mathrm{H}$ NMR($\mathrm{CDCl_3}$) δ 3.86 (s, 6H, $\mathrm{OCH_3}$), 7.4 (broad s, 2H, NH); MS m/z (rel. intensity) 15 (100), 58 (60), 86 (6.6), 101(7.7)

6) **2**: Bp 98 °C; IR (neat) ν 3270, 1650, 1450, 1320, 1070 $\mathrm{cm^{-1}}$; $^1\mathrm{H}$ NMR($\mathrm{CDCl_3}$) δ 3.45 (s, 6H, $\mathrm{OCH_3}$), 2.86 (broad s, 1H, NH), MS m/z (rel. intensity) 15 (100), 44 (61), 58 (35), 59 (40), 89 (3.5).

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