Anodic Oxidations. I. The Electrochemical Cyanation of 2,5-Dimethylfuran

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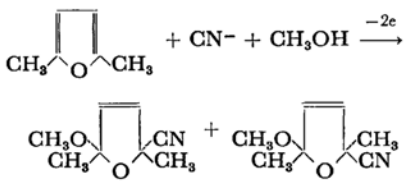
Koyama and co-workers developed a method for the electrochemical cyanation of aromatic compounds.[1-4] With the exception of anisole, however, this method affords very poor yields of aromatic nitriles, and according to circumstances methoxylation is predominant. An improved approach to cyanation of aromatic compounds has recently been reported by Andreades and Zahnow.[5] Cyanation of olefins has also been studied without much success.[3,6,7]

We wish to report a new cyanation reaction of 2,5-dimethylfuran to olefinic cyano ethers.



The over all reaction involves the attack of the cyanide ion on an anodically generated electrophilic intermediate.

Electrolysis was carried out by using a two-compartment cell which was equipped with a platinum wire electrode in the cathode compartment, and with the saturated calomel reference electrode and a platinum plate electrode having an area of 8 cm^2 in the anode compartment. A methanolic solution (40 m*l*) of 2,5-dimethylfuran (0.8 M) and sodium cyanide (0.8 M) was electrolyzed at 21°C for 7.5 hr, using an anode potential of 1.3 V *vs.* SCE. The catholyte was a methanolic solution of sodium cyanide (0.8 M). The current was about 60 mA. Vacuum distillation of the electrolyzed mixture afforded 0.92 g of colorless liquid boiling at 80°C/10 mmHg. The products were identified by infrared, mass and NMR spectroscopy to be a 2.4 : 1 mixture of the *cis* and *trans* isomeric 2,5-dihydro-2-cyano-2,5-dimethyl-5-methoxyfurans[8]; the molecular weight 153, the current yield 74%. Found: C, 62.78; H, 7.30; N, 9.06%. Calcd for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14%.

Current-potential measurements were also carried out on a 0.8 M solution of sodium cyanide in methanol at 25°C, both in the presence and absence of 2,5-dimethylfuran, by using the same cell as that used for electrolysis. The measurements clearly showed that at 1.3 V the cyanide ion was not discharged to any discernible extent. Under the present conditions, therefore, it is 2,5-dimethylfuran that has predominantly been discharged at the anode. The electrophilic intermediate thus formed may have then reacted with both cyanide ion and methanol to form olefinic cyano ethers.

One major advantage of the present reaction lies in its relatively high yield in producing cyanated derivatives. Under the experimental conditions here adopted, the current yield was as high as 74% although the total yield of the cyano ethers based on 2,5-dimethylfuran used was *ca.* 20%. Another merit is that the reaction is accompanied by no undesirable side reactions.

Investigations of the mechanistic details of the reaction and its extension to other substrates are now under way and will be reported elsewhere.

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8) The NMR spectra of these products were compared with those of the known 2,5-dihydrofurans and the *cis* configuration was tentatively assigned to the major isomer: a) A. Aito, T. Matsuo and C. Aso, This Bulletin, **40**, 130 (1967); b) A. J. Baggaley and R. Brettle, *J. Chem. Soc., C*, **1968**, 969.