

Electrooxidative Conversion of Aldehydes into Methyl Carboxylates

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Synopsis. The electrolytic oxidation of methanolic solutions of aldehydes in the presence of sodium cyanide at a platinum anode was found to produce corresponding methyl carboxylates.

Several chemical procedures for the preparation of methyl carboxylates from aldehydes in methanolic media using peroxides,¹⁾ ozone,²⁾ or manganese dioxide³⁾ have been reported, but only a few reports are available on the electrooxidative conversion of aldehydes into methyl carboxylates.⁴⁾

Thus, we wish to report here the electrochemical oxidation of aldehydes⁵⁾ in methanol containing sodium cyanide, which can afford methyl benzoates in good yields.

Results and Discussion

Table 1 shows the results of the electrooxidation of several aldehydes in methanolic sodium cyanide on a macro-scale. These electrolyses were performed in a divided cell at room temperature using a platinum gauge anode under constant current conditions until almost all of the aldehyde was consumed.

Generally, aromatic aldehydes readily underwent anodic oxidation and were converted into the respective methyl benzoates. As an example of the oxidation of benzaldehyde, the ester yield at the stage where 2F/mol of electricity passed was 62%, and by passing an excess of electricity it reached approxi-

mately 90%, according to GLC analysis. From the resulting anolyte, essentially pure methyl benzoate could be isolated by simple distillation in a yield of 80%. Chemical side reactions such as benzoin condensation rarely took place under the present conditions in spite of the reaction in the presence of sodium cyanide.

Similar results were obtained in the oxidation of substituted benzaldehydes with a methyl group or chlorine atom in an *ortho* or *para* position. The yield of their esters was hardly affected by the substituent and its position. However, *p*-methoxybenzaldehyde afforded methyl *p*-methoxybenzoate in yield less than 50% along with the nuclear cyanation product of the ester in yield *ca.* 15%.⁶⁾

Attempted oxidation of aliphatic aldehydes by the same procedure gave only about a 40% yield of the methyl carboxylates and a considerable amount of a highly viscous liquid which may be derived from aldol condensation.

The aldehydes were more oxidizable in methanolic sodium cyanide than in a lithium perchlorate-acetonitrile electrolyte system, since benzaldehyde was oxidized at the potential of 2.3 V *vs.* SCE in lithium perchlorate-acetonitrile solution in contrast to the potential at about 1.7 V in methanolic sodium cyanide.⁷⁾ Therefore, it was assumed that the anodically oxidized species would not be the aldehyde itself, but its derivatives such as cyanohydrin.

The present reaction seems to proceed by a scheme

TABLE 1. ELECTROOXIDATIVE CONVERSION OF ALDEHYDES INTO METHYL CARBOXYLATES IN METHANOLIC SODIUM CYANIDE^{a)}

RCHO R	Oxidation potential <i>vs.</i> SCE ^{b)} V	Anode potential <i>vs.</i> SCE V	Consumed current F/mol	Material yield ^{c)} /%	Collected range Bp θ_b /°C (mmHg)	Reported ¹⁾ Bp θ_b /°C (mmHg)
C ₆ H ₅ -	2.30	1.6—1.8	5.6	80	82—84 (15)	96—98 (24)
2-CH ₃ -C ₆ H ₄ -	2.26	1.8—2.0	6.2	77	97—100 (18)	97 (15)
4-CH ₃ -C ₆ H ₄ -	2.23	1.7—1.9	5.5	83	98—100 (16) mp 32—33 °C	217 mp 33.2 °C
4-CH ₃ O-C ₆ H ₄ -	1.82	1.6—1.9	5.1	48 ^{d)}	123—140 (14) ^{h)}	256 mp 48 °C
2-Cl-C ₆ H ₄ -	2.42	1.6—1.8	6.3	73	110—115 (16)	234
4-Cl-C ₆ H ₄ -	2.22	1.6—1.8	5.7	78	103—106 (15) mp 42—43 °C	mp 44 °C
<i>n</i> -C ₃ H ₇ -	—	1.6—1.9	18.3	(44) ^{e, f)}		
<i>n</i> -C ₇ H ₁₅ -	—	1.7—2.0	18.3	38 ^{g, f)}		

a) Anolyte: aldehyde (50 mmol) and NaCN (75 mmol) in 160 ml of MeOH. Constant current, 0.8 A. Temperature, *ca.* 17 °C. b) $E_{1/2}$, measured in 0.25 mol dm⁻³ LiClO₄-MeCN containing the aldehyde in concentration of 5 × 10⁻³ mol dm⁻³ with a voltage scanning rate of *ca.* 0.1 V/s at a platinum electrode. c) Based on aldehyde. d) From the residue of the distillate, nuclear cyanation product of the ester was isolated in a yield of *ca.* 15%: mp 124—125 °C, white needles from methanol; IR ν 2230 cm⁻¹ (CN); MW 191 (mass). e) According to GLC. f) Undistilled viscous liquid was also obtained, but it was not further investigated. g) Isolated by column chromatography on silica gel using benzene as the eluent. h) This fraction was purified by redistillation, bp 132—135 °C (14 mmHg), mp 45—47 °C. i) Ref. 8.

analogous to that of the oxidative conversion of aldehydes into esters with manganese dioxide and sodium cyanide,³⁾ in which the initial step is the formation of cyanohydrin, followed by oxidation to acyl cyanide which can readily react with alcohol to form the ester.

In fact, a similar electrolysis of mandelonitrile gave methyl benzoate in a reasonable yield, but the ester was scarcely obtainable by anodic oxidation of benzaldehyde using sodium perchlorate or tetraethylammonium *p*-toluenesulfonate in place of sodium cyanide as the supporting electrolyte.

Apparently, the cyanide ion played an important role in this reaction; however, the exact catalytic behavior could not be recognized, because the consumption of the cyanide ion was confirmed. Consequently, an excess of more than an equivalent of sodium cyanide to the aldehyde should be used to obtain the ester effectively.

This electrolysis was not applicable to α,β -unsaturated aldehydes such as cinnamaldehyde or 2-methyl-2-pentanal under the present experimental conditions. In these cases, many unidentified miscellaneous products were formed.

Experimental

The macro-scale electrolyses were carried out in a 200 ml beaker separated from the cathode compartment by a glass filter. The anode was a cylindrical platinum gauge (4.5 cm in high, 11 cm in circumference, 55 mesh), and the cathode was a platinum coil (0.8 mm ϕ , 20 cm). The cell was externally cooled with water, and the anolyte was stirred by a magnetic stirring bar.

The general procedure is as follows. A solution of benzaldehyde (50 mmol) in methanol (160 ml) containing sodium cyanide (76 mmol) was electrolyzed at a constant current of 0.8 A for 9.4 h. After completion of the reaction, the solvent was distilled off, and the residue was washed with

water, followed by dual extraction with ether. The combined extracts were concentrated on a water bath, and the warm residue was vigorously shaken with a small quantity of saturated sodium hydrogensulfite solution. The oily layer was extracted with ether, and then distilled under reduced pressure after dehydration with anhydrous sodium sulfate.

Identification of products was made by infrared spectroscopy and comparison with authentic samples prepared by the usual manner.

References

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- 2) P. Sundararaman, E. C. Walker, and C. Djerassi, *Tetrahedron Lett.*, **1978**, 1627.
- 3) E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Am. Chem. Soc.*, **90**, 5616 (1968).
- 4) To the best of our knowledge, only one paper has previously showed that the anodic oxidation of benzaldehyde in methanolic sodium methoxide gives methyl benzoate; however, the yield was less than 30%: M. Tatsumi, Japan Patent, 68 14683 (1968); *Chem. Abstr.*, **71**, 70336d (1969).
- 5) For a review of anodic oxidation of aldehydes, see: N. L. Weinberg and H. R. Weingerg, *Chem. Rev.*, **68**, 449 (1968).
- 6) The same product was obtained in a poor yield in an anodic oxidation of methyl *p*-methoxybenzoate in methanolic sodium cyanide.
- 7) Addition of significant amounts of the aldehyde to the electrolyte brought about a remarkable increase of electrolytic current at higher cathodic potentials rather than the potential of methanolic sodium cyanide without aldehydes.
- 8) "Dictionary of Organic Compounds," 4th ed, ed by J. R. A. Pollack and R. Stevens, Eyre and Spottiswoode (Publishers) Ltd., Great Britain (1965).