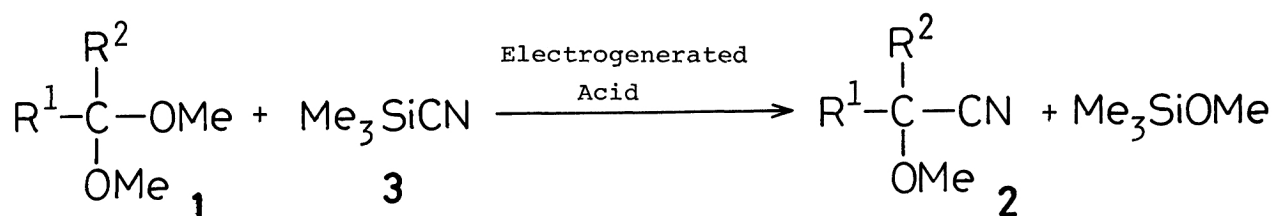


ELECTROGENERATED ACID AS AN EFFICIENT CATALYST FOR CYANATION OF ACETALS WITH TRIMETHYLSILYL CYANIDE

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A facile cyanation of acetals with trimethylsilyl cyanide, giving the corresponding α -alkoxyalkanenitriles, is achieved by using an electrogenerated acid as an acid-catalyst.

α -Alkoxyalkanenitriles, a protected form of cyanohydrin, are synthetically useful compounds as precursors of 3-amino-2-alkenenitriles¹⁾ and α -alkoxyketone²⁾ and as a synthon of acyl carbanion equivalents.³⁾ Although the preparation of α -alkoxynitriles by means of cyanation of acetals with trimethylsilyl cyanide has been recently reported,⁴⁾ a highly convenient procedure which can be conducted under almost neutral conditions is still required owing to extremely toxic nature of cyanating reagent. In continuation of studies on organic transformation with an electrogenerated acid,⁵⁾ we have described here a facile cyanation procedure of dimethyl acetals with trimethylsilyl cyanide promoted by electrolysis.

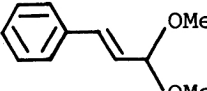
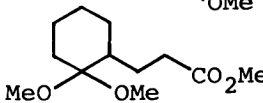
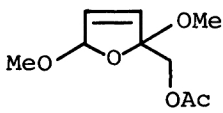
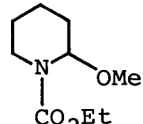


A typical experimental procedure is exemplified by the preparation of 2-methoxyoctanenitrile 2a. A mixture of heptanal dimethyl acetal 1a (541 mg, 3.38 mmol), trimethylsilyl cyanide (0.7 ml, 5.26 mmol), LiClO₄ (23 mg), and Et₄NClO₄ (52 mg) in CH₂Cl₂ (5 ml) was electrolyzed with platinum electrodes (1.5 cm²) in an undivided cell at an applied voltage of 15 V (current: 12-13 mA).⁶⁾ After electrolysis for 32 min (electricity: 0.077 F/mol based on acetal 1a) and stirring for additional 5 min, the reaction was quenched with pyridine (2 drops). Concentration in vacuo followed by either column chromatography (SiO₂, hexane-AcOEt 50:1) or bulb to bulb distillation gave the cyanide 2a in 89% yield.

As shown in Table 1, most acetals of aldehydes and ketones could be smoothly converted into the corresponding cyanohydrin methyl ethers 2 with a catalytic amount of electricity. Cyanation of acetals of cyclic structures 1i and 1j proceeded through the replacement of methoxyl group to give 5-cyano-2-methoxy-2-acetoxymethyldihydrofuran 2i and 2-cyanopiperidine 2j, respectively. Electrolysis with either LiBF₄ or Et₄NOTs as a supporting electrolyte resulted in the recovery

of starting acetals 1. Further application of the electrogenerated acid to organic transformation is now under progress.

Table 1. Electrochemical Cyanation of Acetals 1^{a)}

Acetal <u>1</u>	<u>3</u> , equiv.	Time/min (F/mol) ^{b)}	Yield ^{c)} of <u>2</u> /%	Bp θ_b /°C (Torr) ^{d)}
$\begin{array}{c} R^1 \\ \diagdown \\ C \\ \diagup \\ R^2 \end{array} \begin{array}{c} OMe \\ \diagup \\ C \\ \diagdown \\ OMe \end{array}$				
a) $R^1 = C_6H_{13}, R^2 = H$	1.6	32 (0.077)	89	85(9)
b) $R^1 = Ph, R^2 = H$	1.5	35 (0.043)	80	105(9)
c) $R^1 = PhCH_2, R^2 = H$	1.6	12 (0.029)	87	110(9)
d) $R^1 = 2\text{-Furyl}, R^2 = H$	1.4	1 (0.014)	82	105(9)
e) $R^1 = MeO_2CCH_2, R^2 = H$	1.6	18 (0.150)	72	75(5)
f) $R^1 = C_6H_{13}, R^2 = Me$	1.5	10 (0.061)	80	
g) 	1.5	32 (0.398)	81	90(3)
h) 	1.5	15 (0.056)	93	91(3)
i) 	1.5	22 (0.192)	88	76(3)
j) 	1.5	30 (0.28)	75	83(3)

a) Carried out using 1 (0.5-3.4 mmol) and 3 (0.75-5.3 mmol) in CH_2Cl_2 (5 ml) under an applied voltage of 15 V (current: 5-13 mA) at room temperature.

b) Electricity based on 1. c) Isolated yield. d) Indicated by an air-bath temperature without correction.

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- 6) Usually, ca. 2-8 mol% of $LiClO_4$ (vs. acetal 1) was used.

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