Communications to the Editor

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A SIMPLE ELECTROCHEMICAL OXIDATION OF ALDEHYDE ACETALS TO ESTERS IN NEUTRAL SOLUTION

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Anodic oxidation of aldehyde acetals to esters under very mild conditions is achieved in a neutral solution by utilizing N-hydroxyphthalimide as a mediator. The oxygen source of the oxidation is thought to be not dioxygen but water.

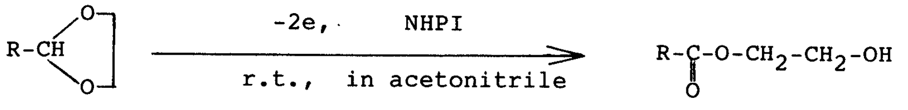
KEYWORDS——acetal; anodic oxidation; mediator; N-hydroxyphthalimide; ester; glyceride

Not a few papers have reported the electrochemical oxidation of aldehydes.[1a,b] However, except in the cases of only a few kinds of aldehydes,[1a,b,2] the oxidation generally requires a very high electrode potential, and production of the carboxylic acids is poor and given in unspecified yield among many other degradation products. When the solution is strongly basic, a lower oxidation potential is applicable. In this case the electroactive species produced in the system are $R\text{-}CH(X)O^-$ (X is OH or CN), but the yields of carboxylic acids or esters are still rather poor and still some side-reaction products are produced.[2,3,4] The electrochemical oxidation of glucose to gluconic acid[5] and glyoxal to glyoxylic acid[6] in the presence of halide ions, with appreciable yield, is the well known oxidation by halogen generated electrochemically. Oxidation of acetals to esters are only performed by various oxidizing agents.[7] The oxidation of aldehydes, including the corresponding acetals, to carboxyl functions by the electrochemical method is, at present, commonly believed to be inadequate from the synthesis point of view.

Satisfactory electrochemical deprotection of ketone acetals was first achieved by a combination of 1-phenylethane-1,2-diol as a protecting reagent and N-hydroxyphthalimide as a mediator.[8] However, the method was not applicable for aldehyde acetals, because the oxidation of the aldehyde occurred predominantly.

Investigation of the oxidation revealed that the electrochemical oxidation of acetals, easily derived from aldehyde, in the presence of N-hydroxiphthalimide (NHPI) produced esters for the first time in excellent yield in neutral solution under simple, and mild conditions.[9]

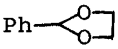
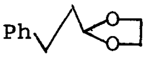
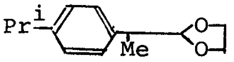
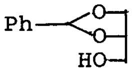
The reaction is illustrated by equation (1).



$$R\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH \quad (1)$$

(I) (II)

Table. Yields of Esters from Aldehyde Acetals a)

	Aldehyde acetals	Yield of esters (%)	Acetals recovered (%)	F/mol b)
1		31	39	2
2		93	-	2
		95 c)	-	2
3		100	-	2
4		83	-	2
		47	-	3
5		84	-	2
6		46	0	2
7		49	26	1
		39	Trace	2
8		54	44	2
9		9 d)	-	2
10		80 d, e)	-	2

a) Determined by GLC .

b) Electricity passed per mole of acetal.

c) Under N_2 gas.

d) Isolated yield.

e) Mixture of 1- and 2-benzoyl glycerols (7 : 3).

The oxidation product (II) is easily hydrolyzed to give carboxylic acid and glycol. Thus the reaction may also be utilized to obtain carboxylic acid from aldehyde, monoacylation products of glycols, and to remove alkylidene and benzylidene protecting groups from glycols. Results are shown in the Table.

The oxidation is believed to proceed via hydrogen abstraction from the aldehyde carbon by phthalimide N-oxyl (PINO) generated at the glassy carbon anode.[8,10,11] 1,3-Dioxolane is more susceptible to the reaction than dimethylacetal and the 1,3-dioxanes [(1), (2), (4), (8) and (9) in the Table]. PINO is active in the oxidation of benzyl derivatives,[8] alcohols,[10] and olefins,[11] but in the present case the abstraction of hydrogen from aldehyde carbon seems to be prefered more than from others [(5) and (10) in the Table]. In the oxidation of those compounds overoxidation must be cautiously avoided [(4) and (7) in the

Table]. The presence of dioxygen seems unnecessary, and the oxygen source is, therefore, thought to be water [(2) in the Table].

From the results of (10), it appears that the method promises to be useful for the mono acylation of carbohydrates.

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9) Compounds (1) - (10) (20 mM), NHPI (5 mM), pyridine (5 mM) dissolved in acetonitrile (20 ml) cotaining ca. 0.1 M $NaClO_4$ were electrolysed potentiostatically (0.85 V vs. SCE) in an undivided cell using a glassy-carbon plate electrode (1 X 3 cm) at room temperature until 1.0 or 2.0 F per mol of acetals had been consumed. Evaporation followed by silica gel column chromatography of concentrated solutions of the residue in chloroform gave the esters. The structures of the products were confirmed by ^{1}H-NMR comparison with authentic samples.
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