Electrochemical methoxylation of vinyl ethers: a novel anodic dimerization reaction

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Electrolysis of vinyl ethers in methanol using a platinum anode and nickel cathode was found to yield the corresponding 1,2-dimethoxylation products (60–66%) and products resulting from a tail-to-tail dimerization to succindialdehyde acetals (20–22%). A mechanism involving radical cation intermediates is proposed.

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We have previously reported the electrochemical methoxylation of the isomeric dimethoxybenzene to *o*- and *p*-benzoquinone ketals (1), a class of substances inaccessible by other methods. Since benzene, simple ethers, and olefins react sluggishly or not at all under conditions which readily produce benzoquinone ketals from dimethoxybenzenes, it occurred to us that the only structural requirement in the latter for smooth anodic methoxylation could consist in the presence of vinyl ether units. Accordingly, a variety of aliphatic vinyl ethers were submitted to the conditions of electrochemical methoxylation described previously (1) using the same type of electrolysis cell (two concentric platinum gauze anodes and a nickel cathode; 1–0.5% KOH in methanol as the solvent). This work led to the discovery of two novel reactions of considerable practical and theoretical interest: (*a*) the dimethoxylation of the olefinic bond of vinyl ethers; and (*b*) the *dimerization* of vinyl ethers to succindialdehyde acetals.

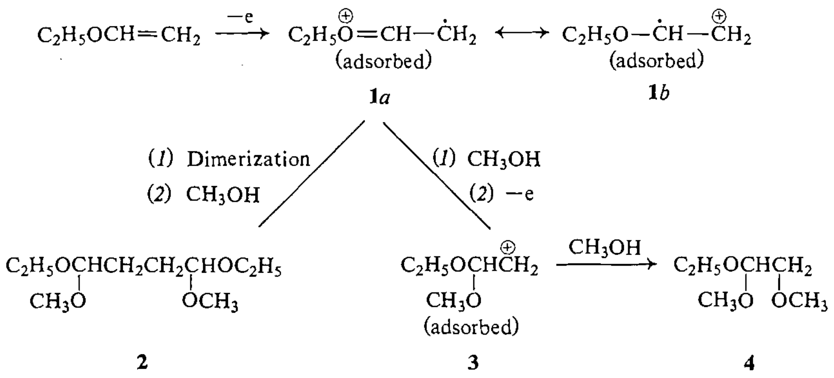
A typical procedure was as follows. A one-litre electrolytic cell (160 cm^2 platinum gauze as anode and 240 cm^2 nickel as cathode) was charged with a solution of 42 g ethyl vinyl ether and 800 ml of methanol containing 5 g KOH. While stirring at −5°, a current of 4 A and 7 V was applied ($\sim$0.025 A/cm^2) for 24 h. The methanol was removed by distillation and the residue fractionated *in vacuo* (Todd column 30 cm) to give 1-ethoxy-1,2-dimethoxyethane, b.p. 58°/27 mm, n_D^{25}1.3954 (68% yield), 1,4-diethoxy-1,4-dimethoxylbutane, b.p. 110°/10 mm, n_D^{25}1.4148 (22% yield), and 2,4-dinitrophenylhydrazone m.p. 259–262° (decomp.). Other examples are assembled in Table I where it can be seen that the reaction is of general applicability.

The mechanism of this reaction is of considerable interest. The studies of Zweig *et al.* (2), revealed that the methoxybenzenes have remarkably low half-wave oxidation potentials. Their election spin resonance (e.s.r.) data show that anodic discharge readily produces absorbed radical cations, which they suggest could yield dimerization products. We have been unable to demonstrate this in our previous studies (1), presumably because of the very low discharge potential of the

TABLE I
Products of electrochemical methoxylation of vinyl ethers

Starting vinyl ether*	Dimethoxylation product (as in **4**)			2,2-Dimerization product (as in **2**)		
	Boiling point	n_D^{25}	% yield	Boiling point	n_D^{25}	% yield
Ethyl	58°/27 mm	1.3954	68	110°/10 mm	1.4148	22
Methyl	129–130°	1.3918	60	96°/12 mm	1.4136	20
Butyl	79–81°/12 mm	1.4063	75	92°/0.3 mm	1.4242	15
Δ^2-tetrahydropyran	85°/28 mm	1.4351	66	118°/1.5 mm	1.4684	24
1-ethoxycyclohexene	59°/1 mm	1.4408	66		Not isolated	
Methyl 1-decenyl	97°/1 mm	1.4288	40		Not isolated	

*All new products reported in this table had the correct empirical composition as determined by microanalysis.



methoxybenzene radical cations. It is logical to suggest similarly that vinyl ethers readily discharge at the anode to give the adsorbed radical cation **1***a* ↔ **1***b*. Subsequently, **1***a* would dimerize to yield **2** after reaction with the solvent, but for reasons unknown as yet, the resonance form **1***b* does not give dimerization products. Alternatively, **1***a* would react rapidly with the solvent but would simultaneously discharge to give cation **3** which would finally yield **4** after reaction with the solvent. We feel that this mechanism accounts adequately for the substrate specificity of the anode in this reaction and for the observed products. Only one other anodic dimerization reaction in the non-aromatic series has general utility: the Kolbe synthesis (3). The anodic dimerization of vinyl ethers (**1***a* ↔ **2**) constitutes a second example which, because of the nature of the products, may have broader synthetic utility.

Acknowledgments

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A revised structure for the so-called "diadrenaline ether"[1]

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The correct structure for the product, obtained by the action of 20% HCl on adrenaline (**1**) and previously described as diadrenaline ether (**2**), has been shown to be 6-(3′,4′-dihydroxy-α-methylaminomethylbenzyl)adrenaline (**3**). The trivial name adrepine is suggested for the base (**3**).

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In 1923 Funk and Freedman obtained a crystalline product (m.p. 180–183°) from adrenaline (**1**) by the action of ethanolic hydrogen chloride at reflux temperatures (1). These authors proposed the "diadrenaline ether" (**2**) structure for this compound (isolated as the dihydrochloride) essentially on the basis of microanalytical data and its color reactions. Several years later Öppinger and Vetter obtained the

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