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## **Electrochemical Fission of Vicinal Diketals to Orthoesters**

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Anodic methoxylation at a platinum electrode of  $\alpha, \alpha'$ -dimethoxystilbene yielded benzil tetramethylketal (2) which upon further electrolysis in methanol gave a 62% yield of trimethyl orthobenzoate. The mechanism of this new anodic fission reaction is briefly discussed.

La méthoxylation anodique, sur une électrode de platine, de l' $\alpha,\alpha$ -diméthoxystilbène conduit au benzile tétraméthylcétal (2) qui par électrolyse ultérieure dans le méthanol donne le triméthylorthobenzoate, avec un rendement de 62%. Le mécanisme de cette nouvelle réaction anodique de fission est discuté brièvement. [Traduit par le journal]

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During the course of our studies on the electrochemical synthesis of benzoquinone ketals, it was observed that *o*-benzoquinone tetramethyl ketal possessed the remarkable ability to suffer anodic cleavage in alkaline methanol to the corresponding hexamethyl cis, cis-orthomuconate (1). Because of the unprecedented nature of the reaction, the question arose as to whether this anodic cleavage is substrate specific or applicable to other types of vicinal diketals. Accordingly, we chose to test the behavior of an open-chain analog such as benzil tetramethyl ketal (2) which may be expected to yield methyl orthobenzoate (3) upon electrochemical oxidation in alkaline methanol. Unfortunately, the benzil diketal 2 is unknown and could not be prepared by the general methods familiar to the organic chemist. However, by taking advantage of our recent finding that vinyl ethers can be not only dimerized but 1,2-dimethoxylated directly at a platinum anode in methanol (2), an electrochemical synthesis of 2 from  $\alpha, \alpha'$ -dimethoxy stilbene (1) could be envisaged. The starting stilbene 1 can be prepared by first reacting benzil with sodium followed by reaction of the diketyl anion intermediate with dimethyl sulfate (3). The pure product is obtained in low yield and should have the cisconfiguration according to Bauld (4).



Oxidation of 1 in 1% methanolic potassium hydroxide at a platinum anode following our previously described techniques (1, 2) gave after 1 h (3 A, 12 V) the *bis*-ketal 2 (45% yield) and trimethyl orthobenzoate (3) (18% yield). Under the same conditions, the *bis*-ketal 2 underwent electrolytic cleavage to 3 in 62% yield after a reaction time of 1.5–2 h. Optimum conditions for the production of 2 from 1 or 3 from 2 were not determined. The anodic fission of *o*-benzoquinone ketals (1) can thus be

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extended to other vicinal diketals. The question of mechanism is of considerable interest as it bears analogy to the periodate and lead tetraacetate cleavage of vicinal diols and related structures. We have previously shown that adsorbed species at the anode provide the substrate for the solvent methanol (2). In the case of vinyl ethers, the adsorbed species were deduced to consist of radical cations on the basis that dimerization to succindialdehyde acetals is a major reaction pathway. Indeed, radical cations were shown to be generated from methoxybenzenes upon anodic oxidation to quinone ketals (5). However, anodic discharge of 2 cannot yield a resonance stabilized radical cation as is the case with vinyl ethers which benefit from  $\pi$ -conjugation (2). Moreover, we have also eliminated the involvement of methoxy radicals in the production of quinone ketals from methoxybenzenes (5). A mechanism involving initial discharge of a benzene ring to a radical cation subsequently allowing C-C fission through intramolecular electron shifts may also be ruled out since in the absence of methoxy or hydroxy substituents, benzene rings do not suffer anodic oxidation under the experimental conditions (6). A mechanism which might account for the results would consist in an electron discharge from an ether oxygen (as in 4) to give a stabilized cation 6 readily captured by methanol and a stabilized radical 5 readily oxidized to cation 6. One factor which may supply part of the driving force for the fission would be the strong steric repulsion between the four ether oxygens of the  $\alpha$ -diketal. Of considerable interest is the formal analogy of this new C-C fission reaction to the wellknown periodate or lead tetraacetate cleavage of vicinally oxygenated C-C bonds. This new

reaction is potentially useful for the synthesis of mixed orthoesters, a class of compounds not accessible by conventional methods.

## Experimental

## Benzil Tetramethyl Diketal (2) and Trimethyl Orthobenzoate (3)

A solution of 4.8 g of  $\alpha, \alpha'$ -dimethoxystilbene (1) (3) in 250 ml of methanol containing 2.5 g of potassium hydroxide was electrolyzed for 1 h by passing a 3 A current at 12 V while stirring and cooling to 10-15°. A platinum anode (total surface area of 160 cm<sup>2</sup>) and nickel cathode (total surface area of 240 cm<sup>2</sup>) were used as previously described (1, 2). The anodic current density was of the order of 0.03 A/cm<sup>2</sup>. The solvent was evaporated, the residue taken up in ether, and the extract washed with water. Evaporation of the ether yielded an oil which was distilled in vacuo to give 1.20 g (18% yield) of trimethyl orthobenzoate (3), b.p.  $46-8^{\circ}/0.25$  nm (n.m.r. absorption at 6.99  $\tau$  for OCH<sub>3</sub> and 2.68  $\tau$  for aromatic protons in a ratio of 9:5) followed by 2.70 g (45% yield) of benzil tetramethyl diketal (2), b.p.  $112^{\circ}/0.25$  mm (n.m.r. absorption at 6.70  $\tau$  for OCH<sub>3</sub> and 3.00  $\tau$  for aromatics in a ratio of 12:10; TMS as internal reference; CCl<sub>4</sub> as solvent). The overall current efficiency was approximately 45%. Treatment of 2 in aqueous methanol with a little dilute hydrochloric acid gave a quantitative yield of methyl benzoate (identified by i.r. and n.m.r. spectroscopy).

Further electrolysis of 1 g of 2 under the same conditions for 1.5-2 h gave after work-up and distillation a 62% yield (about 5% current efficiency) of trimethyl orthobenzoate identified as above.

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