amalgam. We propose that the electrolytic process forms an amalgam, which is consumed by reducing benzene.

$$TBA^+ + e + Hg \rightarrow TBA(Hg)_n$$

$$Ar + TBA(Hg)_n \rightarrow Ar^- \cdot + TBA^+ + Hg$$

$$Ar^- \cdot \cdots \rightarrow ArH_2$$
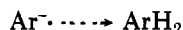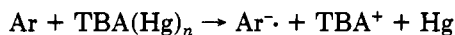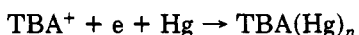
Thus, the electrolyte plays a catalytic role. TBAOH seems to serve a further important purpose by providing an aqueous medium with a high hydrogen overvoltage. UV studies indicate that the electrolyte also increases the solubility of the organic substrates in the aqueous layer by acting as a phase-transfer agent for the aqueous and organic phases that constitute the reaction mixture.

To summarize, we have shown that electrochemical reduction of methoxyaromatics, including steroids, is possible. The products in high chemical yield are the corresponding 1,4-dihydro derivatives. We have presented evidence that the reaction is an indirect electron transfer, possibly involving a tetrabutylammonium amalgam as an intermediate.

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Catalytic Synthesis of Oxalate Esters

Summary: A new catalyst system, palladium(II) acetate, cobalt(II) acetate, triphenylphosphine, and 1,4-benzoquinone, produces oxalate esters in high selectivity from carbon monoxide, oxygen, and alcohol. Up to 140 mol of dimethyl oxalate is obtained per mole of palladium while only traces of dimethyl carbonate or methyl formate are formed.

Sir: The oxidative coupling of carbon monoxide in the presence of alcohol to yield oxalate esters has been known for several years (eq 1).[1] Palladium is the metal of choice

$$2CO + 2ROH + 0.5O_2 \rightarrow ROC(O)C(O)OR + H_2O \quad (1)$$

for this conversion, and systems both stoichiometric[2] and catalytic[3,4] in palladium are known. While the stoichiometric reaction produces oxalates in good yield, most of the catalytic conversions suffer from the simultaneous formation of formate and carbonate esters. An exception is the related heterogeneous palladium-catalyzed conversion of nitrite esters to oxalate esters reported by workers

at Ube Industries.[5] Although oxalic acid is now produced on a moderate scale, oxalate esters are primarily of industrial interest as intermediates in the syngas-based route to ethylene glycol (eq 2).[6] This communication describes

$$ROC(O)C(O)OR + 4H_2 \rightarrow HOCH_2CH_2OH + 2ROH \quad (2)$$
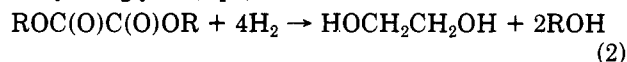
a highly selective catalyst system for the formation of oxalate esters from carbon monoxide, alcohol, and oxygen.

The high-yield stoichiometric conversion of carbon monoxide, methanol, and palladium(II) to dimethyl oxalate has recently been reported.[2] Rivetti and Romano have reported that above 50 °C and under moderate carbon monoxide pressure (300–750 psi), bis(triphenylphosphine)palladium(II) acetate in methanol cleanly produces dimethyl oxalate and acetic acid while being reduced to a mixture of palladium(0) carbonylphosphines. Below 50 °C no reduction occurs, but an intermediate methoxycarbonyl addition product can be isolated (eq 3).

$$(Ph_3P)_2Pd(OAc)_2 + CO + MeOH \rightarrow$$
$$(Ph_3P)_2Pd(OAc)[C(O)OMe] + HOAc \quad (3)$$
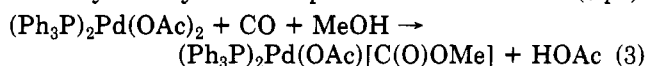
The effect of other phosphines, carbon monoxide pressure, and base on the rate and selectivity has been reported for this conversion.[7]

For a system to be catalytic in palladium, some other stoichiometric oxidant must be present. Quinones are well-known oxidants capable of oxidizing palladium(0) to palladium(II). However, in conjunction with palladium(II) chloride as catalyst, Fenton and Steinwand have reported very low yields of diethyl oxalate when benzoquinone was used as the stoichiometric oxidant.[1] In contrast, in the present work it has been found that high yields of oxalate esters can be obtained with catalytic amounts of bis(triphenylphosphine)palladium(II) acetate. With 0.5–2 mol% of catalyst at 60–80 °C under 1000 psi of carbon monoxide, yields of 60–95% on the basis of 1,4-benzoquinone are obtained.[8] The reaction time and temperature can be reduced if 10–25 equiv (based on palladium) of acetic acid are included.

Although this reaction is clean and highly selective, it is not without problems. Little or no catalysis is seen in the absence of triphenylphosphine, which is removed from the reaction solution by the known Michael addition to benzoquinone.[9] Furthermore, the phosphine–quinone adduct also undergoes Michael addition to benzoquinone to yield an insoluble polymer. Thus, oxalate yields can be variable, depending on the extent of these unrelated side reactions, and this system is unlikely to find any commercial application.

The preferred stoichiometric oxidant for any large-scale application of the oxalate synthesis is oxygen. A number of systems have been described, primarily in the patent literature, that utilize oxygen for the catalytic synthesis of oxalate esters from carbon monoxide.[4] Generally, these systems employ a second metal cocatalyst that in its higher oxidation state will oxidize palladium(0) to palladium(II) and that will be returned to the higher oxidation state by

(1) (a) Fenton, D. M.; Steinwand, P. J. U.S. Patent 3 393 136, 1968. (b) Fenton, D. M.; Steinwand, P. J. *J. Org. Chem.* **1974**, *39*, 701.

(2) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323.

(3) (a) Zehner, L. R.; Sauer, R. W.; Heffron, J. J. U.S. Patent 4 005 128, 1977. (b) Nishimura, K.; Uchiumi, S.; Fujii, K.; Nishihira, K.; Yamashita, M.; Itatani, H. *Ibid.* 4 229 589, 1981. (c) Nishimura, K.; Fujii, K.; Nishihira, K.; Matsuda, M.; Uchiumi, S. *Ibid.* 4 229 591, 1981.

(4) (a) Yamasaki, T.; Eguchi, M.; Uchiumi, S.; Iwayama, A.; Takahashi, M.; Kurahashi, M. U.S. Patent 3 994 960, 1976. (b) Zehner, L. R. *Ibid.* 4 005 129, 1977. (c) Yamasaki, T.; Egushi, M.; Uchiumi, S.; Nishihiro, K.; Yamashita, M.; Itatoni, H. *Ibid.* 4 138 587, 1979.

(5) Tahara, S.; Fujii, K.; Nishihira, K.; Matsuda, M.; Mizutare, K. European Patent Application 0 046 983, 1982.

(6) Sherwin, M. B. *Hydrocarbon Process.* **1981**, *60*, 79.

(7) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1979**, *174*, 221.

(8) A typical procedure is as follows: A stainless steel microreactor was charged with Pd(OAc)₂ (0.03 mmol), Ph₃P (0.09 mmol), 1,4-benzoquinone (3.0 mmol), diglyme (1.6 mmol), methanol (31 mmol), and carbon monoxide (1000 psi). After being heated at 65 °C with gentle shaking for 1 h, the reactor was cooled, pressure was released, and the contents were analyzed by gas chromatography using diglyme as an internal standard. Products formed were dimethyl oxalate (2.5 mmol, 83%), dimethyl carbonate (0.02 mmol, 0.7%), and hydroquinone.

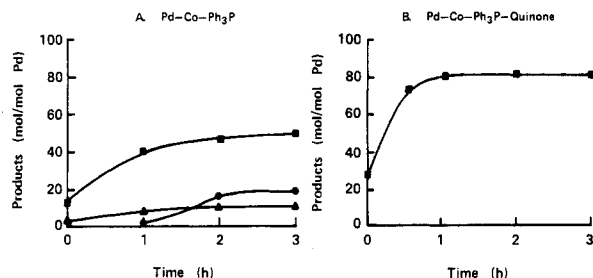(9) Ramirez, F.; Dershowitz, S. *J. Am. Chem. Soc.* **1956**, *78*, 5614.

Figure 1. Effect of catalytic 1,4-benzoquinone on the products of the reaction of carbon monoxide, oxygen, and methanol over a palladium(II) acetate, cobalt(II) acetate, and triphenylphosphine catalyst: dimethyl oxalate (■), dimethyl carbonate (▲), and methyl formate (●). A 300-mL stainless steel autoclave was charged with Pd(OAc)$_2$ (0.50 mmol), Ph$_3$P (1.51 mmol), Co(OAc)$_2$·4H$_2$O (2.00 mmol), methanol (500 mmol), diglyme (10.03 mmol), and methylene chloride to give 100 mL of solution. 1B also contains 1,4-benzoquinone (2.50 mmol). After being flushed with nitrogen, the autoclave was further charged with 1250 psi of carbon monoxide and 75 psi of oxygen and heated with rapid stirring to 90 °C. Products were withdrawn periodically and analyzed by gas chromatography using diglyme as an internal standard. Time zero is defined as the time the reactor reached 90 °C. For each 30 mmol of product, an additional charge of carbon monoxide (75 psi) and oxygen (25 psi) was added to the reactor.

reaction with oxygen. Often these systems are considerably less selective than either the stoichiometric conversion or the previously described system with quinone oxidant and triphenylphosphine-modified palladium(II) acetate catalyst. Part of this loss in selectivity has been blamed on the presence of water,[1,10] a coproduct, and part is due to the known catalytic activity of some of the most effective cocatalysts (e.g., Cu) for the formation of carbonate esters under oxalate-forming conditions.[11] Additionally, the metals most commonly employed [e.g., Cu(II) and Fe(III)] are one-electron oxidants while the palladium oxidation state, by analogy to the stoichiometric reaction, is presumably changing by two electrons.

A large number of cobalt–Schiff base complexes are known to form complexes with oxygen[12] and in some cases have been reported to be oxidation catalysts (e.g., phenol to benzoquinone).[13] Several of these complexes were examined as oxidation cocatalysts in the oxalate synthesis as it was felt that their mechanism of action would be different from that of simple copper or iron salts.[14] Although they do serve as cocatalysts for oxalate formation from carbon monoxide, oxygen, and alcohol, it was found that their behavior is not substantially different from that observed for cobalt(II) acetate, suggesting that the Schiff base oxygen complexes are not a factor. Product formation with time is shown for the palladium(II) acetate, cobalt(II) acetate, and triphenylphosphine (1:3:4 mole ratio) catalyst system in Figure 1A. Although the selectivity for oxalate formation is moderately high for the first hour of reaction, both selectivity and activity drop substantially between 1 and 3 h. The product formation with time shown for this cobalt cocatalyst is not substantially different from that reported for several other systems.[14]

However, a significant improvement in the catalytic oxalate synthesis results from the addition of catalytic amounts of 1,4-benzoquinone to the palladium(II) acetate, cobalt(II) acetate, and triphenylphosphine catalyst. Substantial improvements in the reaction rate, selectivity, and conversion are noted. The rate of product formation with time for the quinone-containing catalyst is shown in Figure 1B. A 3- to 4-fold increase in initial rate is observed over the system with no quinone, and the total amount of oxalate per palladium increases by almost a factor of 2. Most importantly, no more than trace amounts of either carbonate or formate esters are observed. With strongly coordinating solvents such as acetonitrile, as many as 140 mol of dimethyl oxalate can be obtained per mole of palladium before catalyst activity is lost.[14] At least part of the activity can be restored by the addition of more triphenylphosphine. Other ligands more stable to oxidation and less reactive toward quinones have been tried, but none have been found that give the high selectivity of the phosphine-containing catalyst.

In summary, the addition of benzoquinone has been shown to have an important, but as yet unexplained, effect on the initial rate, conversion, and selectivity for the palladium-catalyzed formation of oxalate esters. Similar improvements in the catalyst lifetime require the discovery of a catalyst as selective as phosphine-modified palladium(II) acetate but more stable to deactivation by oxidation.

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Novel Use of Crown Ethers in Chemical Ionization Mass Spectrometry[1]

Summary: Chemical ionization mass spectra of a sample compound S mixed with a crown ether C display abundant (C + H + S)$^+$ ions through selective adduct ion formation when S is an amino acid, purine, pyrimidine, amide, or some other N–H-containing compound.

Sir: Crown ethers[2,3] are characterized by a cavity of a particular size ringed by a number of ether oxygens that complex with cations. The size of the cavity determines which cation would undergo efficient complexation.[4] In the course of a study by chemical ionization mass spectrometry (CIMS) on possible crown ether complexation in the gas phase, we have made several interesting observations.

(10) (a) Zehner, L. R. U.S. Patent 3 992 436, 1976. (b) Zehner, L. R. *Ibid.* 4 005 131, 1977. (c) Zehner, L. R.; Zajacek, J. G. *Ibid.* 4 041 067, 1977. (d) Zehner, L. R.; Zajacek, J. G. *Ibid.* 4 041 068, 1977. (e) Zehner, L. R. *Ibid.* 4 065 490, 1977. (f) Zehner, L. R. *Ibid.* 4 069 388, 1978.
(11) Romano, U.; Tessei, R.; Mauri, M. M.; Rebora, P. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 396.
(12) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(13) Hutchings, D. A. U.S. Patent 3 859 317, 1975.
(14) Current, S. P. U.S. Patent 4 281 174, 1981.

(1) Mass Spectral Studies. Part 13. For Part 12, see: Bose, A. K.; Pramanik, B. N.; Bartner, P. L. *J. Org. Chem.* **1982**, *47*, 4008.
(2) Goldberg, I. "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues", Supplement E1; Patai, S., Ed.; Wiley: London, 1981.
(3) For recent reviews on the complexing properties of crown ethers, see: (a) *Top. Curr. Chem.* **1981**, *98*. (b) De Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279.
(4) Thus, 12-crown-4 binds Li$^+$ strongly, but for efficient binding of the larger ions Na$^+$ and K$^+$, 18-crown-6 has to be used. Potassium acetate, which is insoluble in benzene, can be dissolved in that solvent upon the addition of 18-crown-6. The K$^+$ ion is complexed with all six oxygen atoms and is held inside the cavity ("in the nest" position) while the acetate serves as the gegenion.